Geochemical Prospecting

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The textbook examines the theoretical foundations of geo-chemical prospecting techniques including lithochemical, hydrochemical, atmochemical and biochemical methods. Presents basic principles of lithochemical survey of various scales and a procedure for data quantitative interpretation used in evaluation of minerals' probable reserves. The emphasis is given to ore deposits exploration.
The textbook is intended for geology undergraduates majoring in geochemistry.

Geochemical Prospecting for Mineral Deposits

А. П. Соловов

ГЕОХИМИЧЕСКИЕ МЕТОДЫ ПОИСКОВ МЕСТОРОЖДЕНИЙ ПОЛЕЗНЫХ ИСКОПАЕМЫХ

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Progress in science in the modern world is a matter of the international cooperation and is the result of the joint efforts of many scientists from many countries. This does not mean that we do not recognize the priority and role played by individual researchers in furthering concrete scientific disciplines.

The history of geochemistry dates far back bringing to one's mind the names of the ancient philosophers such as Democritus, Titus Lucrecius Carus and brilliant thinkers of 18th century—Georges Buffon, Mikhail V. Lomonosov, Antoine Lavoisier. We owe the term geochemistry (1842) to the Swiss scientist Christian Friedrich Schönbein. To commemorate the name of the American geochemist F.W. Clarke (1847-1931) in the USSR a science unit, named "clarke" is used to define the average abundance of chemical elements in the geospheres. He earned this honour much as did the Italian Alessandro Volta, the French scientist Ampère, the Britons Michael Faraday and James Clerk Maxwell, the German physicist Georg Simon Ohm and other outstanding natural scientists of the past.

We may name many scholars who were responsible for that geochemistry gradually became a geological discipline by its own right. Undoubtedly, the most important role was played here by the founder of this science, the Russian geochemist V.I. Vernadsky (1863-1945). The principal law of geochemistry as to the "universal occurrence of the chemical elements" formulated by Vernadsky in 1909 is called after him. The wealth of his scientific heritage continues to promote geochemistry. A gold medal to mark his memory has been established by the USSR Academy of Sciences as has an avenue and the Institute of Geochemistry in Moscow been named after him.

Owing to the efforts of N.I. Safronov (1904-1982) modern methods of geochemical exploration for ore deposits emerged in the Soviet Union early in the 1930s. Simultaneously and independently, V.A. Sokolov (1900-1971) proposed a geochemical method of search for oil and gas deposits. Under the guidance of N.I. Safronov, by the efforts of his disciples and followers, geochemical exploration of mineralized areas of the Soviet Union found extensive use and led to the discovery of quite a number of deposits, including very large ones. The 50th anniversary of the fundamental paper by N.I. Safronov

"Concerning dispersion aureoles of mineral deposits" [29] was recently marked by the Soviet scientific community. To perpetuate his name, the "annual Safronov readings" were started in Leningrad. Owing to their high efficacy geochemical methods of prospecting are currently widely used throughout the world. Geochemical exploratory techniques used in the advanced foreign countries that originally relied on Soviet experience have reached now great success. This includes sophisticated procedures of sample analyses and computerized automatic data processing and mapping. Important contributions to geochemical exploration have been made by H.E. Hawkes (USA), J.S. Webb (Great Britain), A.A. Levinson (Canada) and many others. Yet what concerns the theory of geochemical exploration, the Soviet Union is still ahead of foreign countries.

A geochemical exploration for mineral deposit course for students was begun in 1938 in Leningrad and in Moscow. Now, this discipline is part of the curriculum in all geological departments of the Soviet colleges. The present book contains, in fact, the lectures the author has been delivering to students of the Faculty of Geology of the M.V. Lomonosov State University in Moscow since 1964. Apart from these lectures, students of geochemistry do practical work using a problem book [34] and go into the field to familiarize ihemselves with geochemical methods of prospecting. Much attentton is being called in the book to methods of quantitative interpretation of geochemical data which fact makes the book unique among others on the subject.

Among many persons who made possible the apprearance of this book the author is particularly indebted to Professor Dr. E.M. Kvyatkovsky who has read the manuscript and made useful comments.

A. Solovov

Contents

Given below are principal notations used in the present book and recommended for use in literature concerning geochemical exploration and geological records.

A—local parameter determining the shift of a dispersion aureole on a slope

A_x—coefficient of biogenic absorption (capture)

$2a$—effective width of a geochemical anomaly, m

α—angle of inclination of the terrain to the horizon

α'—alluvium slope coefficient

B—coefficient of rock alteration volume upon weathering

$2b$—effective length of a geochemical anomaly, m

β—angle of dip of an orebody, coefficient to determine standard by spread of data

C_C—the clarke value of chemical elements

C_0—background element content

C_x—element content at points on a profile

$\bar{C}_x$—average arithmetic content

$\tilde{C}_x$—average geometrical content

C_{max}—maximum element content in a geochemical anomaly

C_p—element content in the ore

C'_x—element content in a dispersion flow

C_A, C_{A1}—lowest anomalous element content

$C_{A,\,m}$—element content considered anomalous, given m correlating points $(m \leqslant 9)$

d—density (volume mass)

E—ore formation energy

ε—standard factor $(\varepsilon = \text{antlog } s_{\log})$

η—correction factor to convert productivity of a supraore primary halo to the economical ore level

F—force

f—number of tested ore levels

$\Phi\,(x)$—integral of probabilities for limits $\pm x$

γ—contrast index for weak geochemical anomalies (signal-to-noise ratio)

H—vertical distance (in m) to which expected ore reserves are estimated

h—thickness of eluvio-deluvium

h_0—thickness of cover of transported sediments

I—multiplication index

Δh—annual denudation layer

i, j—sequence numbers of letter symbols of a quantity; numbers of observation points

K_x—coefficient of aqueous migration of elements

K_h—concentration clarke

k—coefficient of residual productivity characterizing the ratio between metal square meter percentage in the dispersion aureole and in the primary ore $(M{:}M_p; P{:}P_p; q{:}q_p)$

k'—proportionality coefficient between productivities of dispersion flows and aureoles

$\varkappa$—similarity coefficient characterizing genetically identical deposits of different size

L—length of target of search (geochemical anomaly)

$2l$—distance between profiles of survey grid

$1/\lambda$—migrational capacity (mobility) of an element in a primary halo, m

λ'—correction coefficient to evaluate the true productivity of a lithochemical dispersion flow

M—higher-than-average amount of metal in a profile (linear metal productivity), m %

M_p—amount of metal in the cross section of a mineralized zone. Linear productivity of an ore zone, m %

m, N, n—number of points, samples, frequency etc.

ν—geochemical zoning index—dimensionless ratio between contents of two or more chemical elements of a geochemical anomaly monotonically varying in a specified direction

ω—angle

P—higher-than-average productivity of a geochemical anomaly, m² %

P_p—areal productivity of primary mineralization, m² %

$\sum P_i$—total (stable) productivity of a dispersion flow, m² %

p_x'—apparent productivity of a dispersion flow

$2p, 2p_x$—thickness of an orebody, m

$2p_y$—length of an orebody, m

Π—probability of a random event

Q—quantity (reserves) of metal, t

Q_H—expected (geological) metal resources in ore showings to a depth H

q—amount of metal in a dispersion aureole to a depth 1 m, t/m

q_p—amount of metal in a primary mineralization for a layer 1 m thick, t/m

Δq_p—specific productivity of a mineralization, t/m per km^2

R—distance from the watershed apex to a point of P'_{max}, spread of observations

R_0—distance from the watershed apex to a point where metal starts to be moved to the stream bed from the slope

r—correlation coefficient; radius

S_x—catchment area (denudation basin area), m^2

S_α—displacement of a dispersion aureole downslope, m

S_β—displacement of a dispersion aureole along the rise, m

s—standard deviation

σ—coefficient of supergene dispersion, m

T—time

τ_x—thalassophylic coefficient

x—direction along a profile (across the strike of an orebody), downstream direction along the stream bed

Δx—sampling interval along the profile, m

y—direction along the strike of an orebody

z—direction along the dip of an orebody, normal to the ground surface, depth, m

The indices $x, y, z, 0, h, p, i$ etc. added to letter symbols show that the particular variable or parameter are considered in the given direction (x, y or z), at the ground surface (0), at the boundary of the bedrock (h), in the mineralized zone (p), at a point given the sequence number i etc.

General Principles of Geochemical Exploration

Sec. 1.1. Introduction

The principal and often sole objective of any geological operation, whatever its particular content, is to find materials for the industry. This is made possible by geological, geophysical and geochemical exploration followed by mining and drilling operations. Whatever the stage of geologial prospecting, an important role is played by geochemical methods of the search for mineral deposits.

Modern geochemical methods of exploration have emerged to meet economical requirements and were made possible due to the efforts of pioneers of geochemistry, notably, V.I. Vernadsky (1863-1945), advances in the science concerned with mineral deposits and progress in the analytical techniques. Credit goes to N.I. Safronov (Fig. 1) who elaborated geochemical methods of exploration for ore deposits which date back to 1931-1932 when he, in charge of the section of geophysics of the ZNIGRI, today's VSEGEI, the All-Union Geological Institute, in Leningrad started to work out a physicochemical method of exploration. First field work operations based on this method were successfully carried out in different ore-bearing regions in the USSR. V.A. Sokolov [29] (1900-1971) of Moscow concurrently developed geochemical methods of prospecting for oil and natural gas fields. The newly proposed methods proved highly efficient which led to their extensive use in the USSR and then abroad. Geochemical methods of locating hidden ore deposits are now being applied all over the world.

The Soviet Union ranks first in terms of the amount of applications and the scientific level of the theoretical foundations of these methods. Foreign workers have repeatedly emphasized the priority of Soviet scientists in elaborating geochemical methods of exploration.

Geochemical techniques have been used to discover more than 100 economically important deposits of tin, copper, lead, gold and other metals in the USSR during the recent few decades. It is through the use of geochemical exploration that numerous ore deposits have been located abroad, particularly, in the developing countries.

Today's theory of geochemical exploration represents a self-consistent body of knowledge that exhibits all the features of a separate branch of geology. It has its own subject of study,

its specific procedures of research and relevant terminology. The subject of study of geochemical exploration is the geochemical field and its local anomalies, which, particularly, should be considered as being economic mineral deposits. The techniques of research are geochemical surveys followed by geological, geochemical and physicomathematical interpretation of the data obtained. Questions related to specialized terminology, among others, are being considered in the USSR by the Council for scientific principles of geochemical prospecting for mineral deposits established in 1968 following a joint decision by the Academy of Sciences and the Ministry of Geology of the USSR. It is the function of the Council to coordinate research work in this sphere, convene national sessions and regional seminars and publish their

FIG. 1. N.I. Safronov (1904-1982)

proceedings. International exchange of geochemical methods of mineral exploration is increasingly gaining momentum.

Sec. 1.2. General Principles of Geochemistry

Modern mining industry, extracting various chemical elements from their natural accumulations, requires that the given mineral deposits should meet definite standards in terms of the content of the valuable component, the amounts of the materials to be won and mode of their occurrence from the standpoint of economic geology. This is what is responsible for the general trend in geological survey, prospecting and exploration operations aimed at the discovery of local concentrations of chemical elements with the purpose of selecting targets for economic exploitation. Geochemical exploration provides a technique for pinpointing such concentrations.

The four all-important principles validated by unambiguous experimental findings [30] that underlie geochemical methods of mineral exploration are these:

(a) the universal occurrence of chemical elements in all geospheres;

(b) the continuous migration of elements in time and space;

(c) the diversity of species and forms in which the chemical elements may be found in nature;

(d) the domination of the dispersed phase over the concentrated one, especially for ore-forming elements.

The universal occurrence of the chemical elements has been proved by analyses of the chemical composition of any rock, mineral, natural water, organic compound or man-made material that have found in these latter determinable amounts of most diversified elements alien to their principal composition. Proper analysis has revealed in an optically transparent single crystal of quartz traces of Fe, S, Pb, Cu, As, Au, Ag, Na, K, Mg and of many other elements that have been omitted by the classical formula of the mineral, SiO_2, the presence of which cannot be explained in terms of isovalent or heterovalent isomorphism of the elements. The universal occurrence of elements is proved by their clark values, average contents of chemical elements in the geospheres permitting their interpretation. The abundance of individual elements varies appreciably from one sphere to another (Table 1).

TABLE 1

Principal Chemical Composition of the Geospheres

Geosphere	Major elements	Number of chemical elements	Clarkes, %, total
Lithosphere	O, Si, Al, Fe, Ca, Na, K, Mg, Ti	9	99.48
Hydrosphere	O, H, Cl, Na, Mg	5	99.58
Atmosphere	N, O, Ar	3	99.94
Biosphere	O, C, H, Ca, K, N, Si, Mg, P, S	10	99.96

Note. A biosphere is understood to be a region of habitation of living organisms encompassing the lower strata of the atmosphere, part of the lithosphere and the hydrosphere. Clarke values of the biosphere characterize the average chemical composition of living matter.

Clarke values of most chemical elements, specifically, important for ferrous and nonferrous industries are measured only in thousandths or millionths fractions of a per cent.

The clarke values, however, are statistical quantities and do not imply by definition the necessary presence of all chemical elements in any naturally occurring assemblage, denoting, as they do, minimum amounts of a substance dealt with in geological practice (1 g, 1 ml, 100 mg etc.). The law of universal occurrence of the chemical elements has been formulated by V.I. Vernadsky. He said in his famous speech addressed to the 12th Congress of Russian natural scientists and physicians on 28 December 1909: "As our analytical techniques become more refined, we will discover more elements in each drop or dust particle found on the earth's surface. It appears that the pattern of their distribution is microcosmic. A sand grain

or a drop of water reflects, as it were, the overall composition of cosmos" [35]. V.I. Vernadsky repeatedly attacked this problem pointing out that even with minor amounts of dispersed elements the number of their atoms may be enormous, however small the volume of the material in hand. For example, 1 cm^3 of sea water contains $n \times 10^7$ of atoms of radium if the content of the latter is $n \times 10^{-13}\%$. As a result, modern geochemistry, interpreting the results of chemical analyses aimed at the discovery of some trace element in a sample, rather than say "none present", would say "not found". The latter definition has, essentially, a different meaning. It implies that the content of the element being sought is below the limiting sensitivity of analysis. It concurrently emphasizes the familiar fact as to how difficult it is to obtain "exclusively" pure materials and as to how implausible it is to have them "absolutely" pure. As proposed by N.I. Safronov, the principal law of geochemistry concerning the universal occurrence of chemical elements is called "Vernadsky's law".

The migration of chemical elements is evidenced by large-scale tectonic and magmatic processes transforming the earth's crust and by most intricate chemical reactions taking place in living matter, by the continuous development of the world around us characterizing motion as a form of the existence of matter. The migration of chemical elements is conditioned by a multitude of extraneous factors, in particular, energy of solar radiation, interior energy of the earth, gravity and inherent properties of the elements themselves. The differences in the capacity to migration (mobility) of the chemical elements are what is responsible for their differentiation and appearance of natural associations with variable ratios of constituent elements. This results, despite qualitative uniformity, in the differences and variations in the chemical element contents at any point on the earth. The concentration and dispersion of chemical elements are interrelated and are opposite aspects of the unique process of the migration of elements.

Figure 2 illustrates the movement of earth materials from one environment to another. Mirroring the intrusion of subcrustal magmatic melts, this geochemical cycle is not a closed one and characterizes the permanent development of the lithosphere. It is noteworthy pointing out that endogenic mineral deposits form during magmatic and postmagmatic activity; and various exogenic deposits, during sedimentation. In all geological periods land has been subject to weathering and denudation, the principal result of which is disintegration and decomposition of the previously existing mineral deposits.

The diversity of species and forms of chemical elements is shown by a multitude of naturally occurring chemical compounds, mechanical mixtures and solutions that they form in various aggregate

states and by the variety of physicochemical bonds between the
elements. Apart from the mineral form of occurrence of elements
running into about three thousand species, they often assume non-
mineral forms which is typical of most chemical elements found in
the hydrosphere, biosphere and atmosphere. The occurrence of
chemical elements as discernible minerals, characteristic of the
lithosphere, is complemented by their presence as indiscernible
submicroscopic minerals, isomorphic and non-isomorphic solid
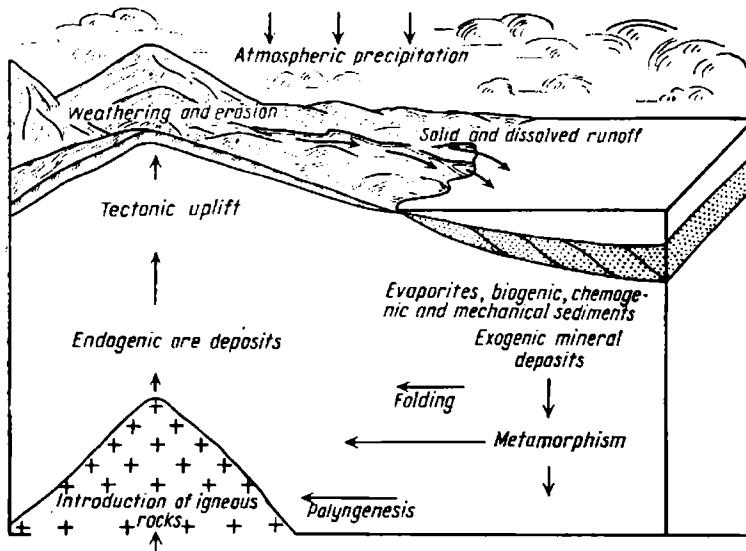
FIG. 2. A scheme of geological cycle of the migration of chemical elements

solutions, acqueous intrarock molecular pellicular solutions or
intracrystalline gaseous and liquid inclusions. Alternatively, they
may be found in the state of sorption and occlusion. The occurrence
of elements in a nonmineral form as indeterminate mineral admix-
tures of variable composition that are not envisaged by their formulae
or stoichiometric relationships is a direct consequence of the univer-
sal distribution of chemical elements.

    The principle of the domination of the dispersed phase over con-
centrated phases of elements needs some clarification. The migration
of chemical elements, in view of the plurality of their species and
forms may give rise to naturally occurring associations exhibiting
practically any (extremely low or very high) content of the element
in question. Element contents equal to 0 and 100% are inconsistent
with Vernadsky's law. For we cannot draw any reasonably correct
boundary line between the dispersed element contents and the high

ones corresponding to a concentrated phase. Such a boundary line would be arbitrary in a series of continuous element contents since we should have to assign different qualitative states to any two adjacent element content values lying on the two sides of the limiting value. Therefore it is reasonable to restrict oneself to a determination of two extreme states taking the element contents approaching its clarke values as being its dispersed phase and ones approaching its contents in natural materials from which the particular element is being economically extracted as being its concentrated phase. Table 2 presents examples demonstrating contents of some elements in a dispersed and concentrated phase. The last column of the table contains approximate ratios of the element contents in the deposit they are being extracted from, C_p, and its clarke value C_C for the particular sphere of the earth. These ratios are referred to as "clarkes of concentration" or concentration ratios and are denoted as K_k.

TABLE 2

Relationships Between a Dispersed and a Concentrated State of Chemical Elements

Name of element	Dispersed state		Concentrated state		Concentration clarke $K_k = C_p / C_C$
	Geosphere	C_C, %	Target	C_p, %	
Fe	Lithosphere	4.65	Orebody	45.0	10
Cu	Ditto	4.7×10^{-3}	Ditto	1.0	200
Pb	Ditto	1.6×10^{-3}	Ditto	1.5	1 000
Hg	Ditto	8.3×10^{-6}	Ditto	0.2	24 000
Br	Hydrosphere	6.5×10^{-2}	Mineral waters	0.4	60
He	Atmosphere	5.2×10^{-4}	Gas deposit	1.0	2 000
H	Lithosphere	0.1	Oil deposit	12.0	120

To appraise qualitative relationships between the dispersed and concentrated phases of elements, N.I. Safronov has estimated total abundances of 11 most important elements found on land to a depth of 1 km as determined by their clarke values and reserves of the same metals found in their deposits (currently exploited, worked out and expected). As a result, even if multiplied by a factor of 40-250, the amount of the known economical reserves proved to be fairly negligible (in %) compared with their total "geochemical reserves" [30]:

copper	4.3×10^{-2}	cobalt	4.4×10^{-4}
lead	1.5×10^{-1}	tin	3.0×10^{-3}
nickel	1.8×10^{-3}	mercury	1.3×10^{-1}

According to independent estimates by McKelvey, the fraction of reserves of important metals to be found in US deposits is in the range from n $(10^{-4}\text{-}10^{-3})\%$ to 0.04% (maximum value) of the total "clarke value" reserves in the lithosphere on the same area to a depth of 1 km.

Summing up what has been presented above, we conclude that the contents of any chemical elements in the geospheres accessible for study are on the average characterized by clarke values; they are always greater than zero, are governed by the coordinates and are not constant in time. The appearance of local concentrations of chemical elements calls for external energy and a combination of advantageous conditions. In the geological cycle of migration of chemical elements (see Fig. 2) such conditions repeatedly arise resulting in the occurrence of deposits of various genetic types. The concurrent appearance of a complex of advantageous conditions needed for the concentration of elements represents a rare geological event. So only a minor fraction of the world's reserves can be found in respective deposits. That is why the discovery of new mineral deposits of economic importance poses rather a difficult geological problem

Sec. 1.3. The Geochemical Field and Its Local Anomalies

The geochemical field is a geological space characterized by values of chemical element contents C_x as functions of the coordinates and time, or

$$C_x = f (x, y, z, T) > 0 \qquad (1)$$

Depending on the nature of the processes conditioning one distribution of the chemical element content and mode of its occurrence or another, Eq. (1) may have different geological and mathematical implications.

The study of the geochemical field consists in measurements of the chemical element contents by collecting geochemical samples at separate sampling points or continuously. The term "sampling" may imply a wide range of operations, from collecting samples followed by analyses or without same, to direct or remote determinations of the chemical composition of natural associations. The chemical element content determinations without collecting samples by using special apparatus are often called "geophysical logging" which also means a method of exploration of the geochemical field.

The results of determinations of the geochemical field are used for the compilation of maps and cross sections in isoconcentrates or for plotting graphs along sampling traverses. A geochemical field may be relatively homogeneous with respect to the chemical element contents, smoothly vary or become complicated by local anomalies. Analysis of the structure of the geochemical field and its quantitative

interpretation, taking into account the geological and geophysical data, allows conclusions to be made in terms of reconnaissance and prospecting.

The values of C_x of the overwhelming majority of points of a geochemical field are approximating the corresponding clarke values and only rarely do they attain values any different from this level. A dispersed phase of elements is their natural, conventional mode of occurrence whereas a concentrated phase represents an anomaly. An orebody is a particular case of a naturally occurring geochemical
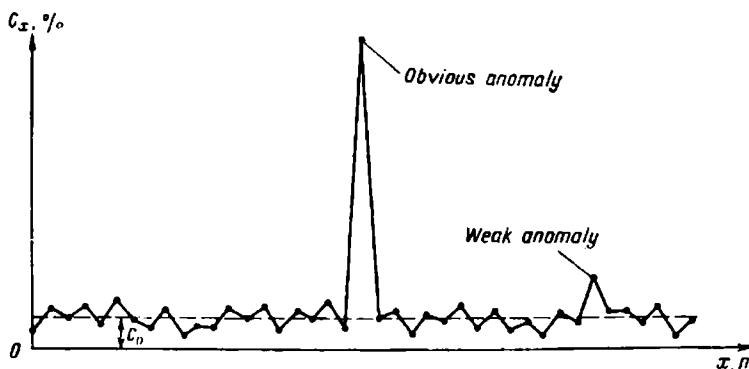
FIG. 3. The plot of geochemical sampling along a profile

anomaly whose total number appreciably exceeds that of economically important deposits. Geochemical prospecting for ore deposits relies upon a search for geochemical anomalies. Concepts of a normal geochemical field and of anomalous element contents are interrelated and call for more detailed analysis.

In the simplest case the results of geochemical sampling of rocks, surface or subsurface waters, plants or soil are conducted across the strike of a linear structure, i.e. along the x-axis, at a constant depth $z = \mathrm{const}$, will not be governed by y and z. In view of the short time taken by our observations compared with the geological time they may be considered as being independent of time T as well. Then Eq. (1) will assume the form of a one-dimensional relationship

$$C_x = f(x) \qquad (2)$$

and will agree with a graph of the given element content determined along a profile of samplings. By assuming a considerable extent of this profile and connecting with a zigzag line the element contents corresponding to sampling points we can easily find large segments of the graphs showing relatively constant and low or background contents of the element C_0 and also rare deviations from this level suggesting geochemical anomalies (Fig. 3). It is not uncommon that

2•

geochemical determinations of many hundreds or even thousands of samples may involve only separate samples pointing to anomalous element content values which is another proof of the fact that the dispersed phase dominates a concentrated one. Even for lengths of traverses in excess of several kilometres the local geochemical background can be rather accurately estimated by referring to graphs of element contents and by drawing an averaging straight line in the region of a stable low mineral content. The method of estimation has been successful since the advent of geochemical exploration and its use is still justified at a stage of preliminary reconnaissance or in a detailed study of an already discovered anomaly. The disadvantage of this method is, first, that the background characteristic is determined only by the averaged value of the element content C_0 without taking into account its consistency and, second, that the choice of the lowest element content assumed to be anomalous is arbitrary. As a result, one is liable to omit a fraction of weaker anomalies or erroneously select fictitious anomalies associated with random variations of the background level. This is the reason why, whatever the geochemical prospecting procedure, more rigorous methods are needed to determine the geochemical background value [17].

Among variations of the general element content as determined along a traverse of samplings we should differentiate *obvious anomalies that can only be determined empirically*. Examples of such kind in sampling of rocks or products of their weathering can be provided by the content of copper 0.3%, lead 0.1 or 0.5%, silver 0.02% etc. Experience shows that such metal contents are not characteristic of these geological formations, so such sampling points, without further discussion, are assumed as being indisputable (obvious) lithochemical anomalies. Based on geological empirical experience, similar unquestionably anomalous contents of ore elements are established for natural waters (e.g. 100 mg/l of Cu or 250 mg/l of Mo etc.), for the chemical composition of plants or for results of gaseous surveys. The *à priori* established concepts of the obvious geochemical anomalies make it possible to infer an idea of *a local geochemical background whose value is assumed to be the average chemical element content within an area of a uniform content away from obvious anomalies*.

Another group of pathfinder element contents deviating from the average level includes *weak geochemical anomalies* to detect which methods of probability statistics are needed. This very approach to interpretation of geochemical data is necessitated by the difference in the element content, in fact, in any two samples including the ore elements content in areas known to be ore-free. Beyond the boundaries of obvious anomalies these variations are of a limited character and are conditioned by a multitude of factors. Areas manifesting departures from the background not falling into a class of obvious

anomalies may be considered as geochemical anomalies only if they exceed the amplitude of local background variations at a specified probability. For a well-founded selection of weak anomalies it is insufficient to have a graphical evaluation of the average element content C_0. Rather, it is necessary also to take into account the range of the local background fluctuations. This important index characteristic is obtained through a statistical treatment of the geochemical data (cf. Sec. 1.5).

To date, natural resources are being generally won from deposits occurring in the lithosphere and referred to lithochemical anomalies. Within such an anomaly it is usual to define the contour of economic ore and a surrounding zone of rocks with a lower content of valuable components insufficient for economic exploitation of such deposits. The zone of higher ore or pathfinder element contents in the country rocks formed at the same time that the orebody formed due to the same processes of endogenic, exogenic (primary deposition) or metamorphogenic mineralization is termed its *primary halo*.

The boundary between an orebody and its primary halo is often not of a geological but temporal, economical character used to distinguish between commerciably extractable ores and marginal grade ores. If we are to revise requirements put on the average metal content in ores and, consequently, on the lowest commercially extractable content, the shape of an orebody in terms of its boundary relative to its primary halo will change accordingly. However, the concept of the primary halo of a deposit is much broader than the current idea of marginal grade ores the outer contour of which is governed only by a lesser than the lowest economic content of the valuable component and which is likely to become a target of commercial exploitation in a foreseeable future. The primary halo includes the ore-bearing zone with the metal content only in a minor way exceeding the local background values and also zones of anomalous contents of pathfinder elements that do not represent valuable ingredients of the deposit. Along the periphery of a primary halo ore element values are asymptotically approaching the background values which complicates the configuration and renders its outer boundary indeterminate. In the contour of a primary halo the geometrical dimensions of a deposit much exceeds in plan and elevation that of the orebody. In the simplest case the primary halo of the principal ore element agrees, within somewhat expanded boundaries, with the shape of the orebody (Fig. 4). Contours of primary halos of a pathfinder element may appreciably differ from the shape of an orebody (see Chap. 4). Any deposit of natural resources, in particular, an oil or natural gas field is enclosed in an halo.

An orebody formed in the deep-seated conditions or buried during sediment accumulation is pushed to the surface by tectonic uplifts and denudation. Figure 4 shows diagrammatically successive posi-

tions of the erosional surface with respect to a steeply dipping lode. The position of the surface at level A shows a mode of blind ore occurrence enclosed in a blind halo. Level B reveals only the aureole (primary halo) above the lode. The erosional surface at level C uncovers both the lode and the enclosing halo. Level D corresponds to a stage at which the lode has already been eroded and the bedrock has preserved only the lower portion of the halo. Further erosion until level E is reached corresponds to a stage where supergene processes have caused the lode and its halo to disappear.

Facilitating access to the deep-seated strata of the lithosphere, weathering and erosion, on the other hand, result in a gradual disintegration of previously existing mineral deposits. The mineral of a deposit, being acted on by agents of weathering and erosion, mixes with the weathering products of the host rocks, becomes dissolved by atmospheric precipitation and undergoes various physicochemical transformations. Chemical elements previously concentrated in an orebody are dispersed in the entire mass of the newly formed loose material and natural waters in the zone of hypergenesis (supergene zone) contributing to the solid and hydrochemical load from land coming to the area of sedimentation and, eventually, to the ocean.
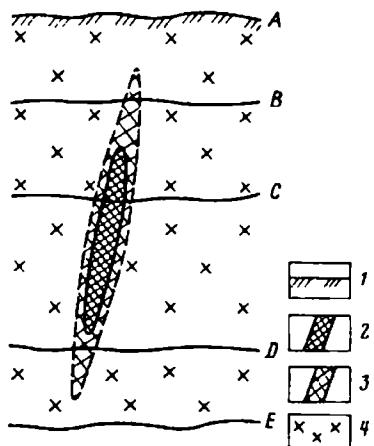
FIG. 4. Horizons of erosional surfaces (B-E) of a steeply dipping orebody and its primary halo:
1—original ground surface; 2—orebody; 3—primary halo from the principal ore component; 4—enclosing rocks

Gaseous products found in the deposit or formed during weathering are dispersed in the atmosphere. Viewed from this standpoint, the upper horizons of modern land where weathering and erosion are at work leading to decomposition and disintegration of previously formed local concentrations of chemical elements are called *the area of dispersion of mineral deposits*. Processes that take place in a zone of dispersion may give rise to local secondary concentrations of chemical elements. This can be illustrated by zones of secondary sulphide enrichment, economically important placers or deposits in the residuum. However, as physicochemical, biogenic or mechanical redeposition of material proceeds giving rise to various secondary element concentrations, an appreciable fraction of useful components is also subject to dispersion. In further relief formation these

secondary concentrations become involved in a new cycle of weathering and erosion, so the process will generally be oriented toward dispersion.

Throughout levels B to D products of weathering known as a regolith are formed containing respective intervals of the valuable component. The resultant zones of increased (anomalous) values of the valuable components or pathfinder elements in the country rocks adjoining the primary ore that form in the course of supergene migration of chemical elements of the mineral deposit are known as *secondary dispersion aureoles*. The chemical element content in secondary halos generally manifests values that are intermediate between high ones in the deposit and lower ones corresponding to the local background. In the first approximation, secondary aureole repeats the planimetric configuration of the deposit and its primary halo as it crops out and generally exceeds these latter in area. A general concept of secondary aureole has been proposed by N.I. Safronov [29] providing a starting point for modern geochemical methods of prospecting.

Areas of higher metal or pathfinder element contents in the channels of transport of solid or dissolved load or gaseous, surface or subsurface runoff from land developing due to secondary aureoles are generally known as *dispersion flows*. Anomalous element contents in dispersion flows show values that are intermediate between high values in secondary aureoles and low local background. A dispersion flow or train is oriented in the direction of the active runoff and may extend to many kilometres from the primary ore gradually diminishing as the chemical element content approaches background or, alternatively, is bounded by the dimensions of the ultimate body of water. With dispersion processes still in progress, geochemical anomalies linked up with physical disintegration and chemical decomposition of the deposit may be discovered in lakes or littoral zones of seas and oceans. Secondary aureoles and dispersion flows may be revealed in different geospheres—in the chemical composition of rocks, products of their weathering and soils, in surface and subsurface waters, in the composition of the subsurface and near-surface atmosphere, vegetation and living organisms. Accordingly, we differentiate between lithochemical, hydrochemical, atmochemical and biogeochemical secondary (supergene) dispersion aureoles and flows. Figure 5 presents the most common correlations between an orebody and its secondary and dispersion aureole and flow under conditions of modern mountain topography. In other cases these correlations are more complicated.

A primary lithochemical halo, a secondary aureole and dispersion flow, owing to their large dimensions and occurrence close to the ground surface are easier to detect compared with a concealed orebody. Therefore the discovery of a deposit is made possible by geo-

chemical methods of search for its primary and secondary halos and dispersion aureoles and flows. There are various highly sensitive methods available for revealing these geochemical anomalies that serve as indications of possible economic ore. So, e.g., lithochemical prospecting for deposit of Au and Hg relies on analyses of rocks with a sensitivity 10^{-7} % which is ten thousand times and two million times
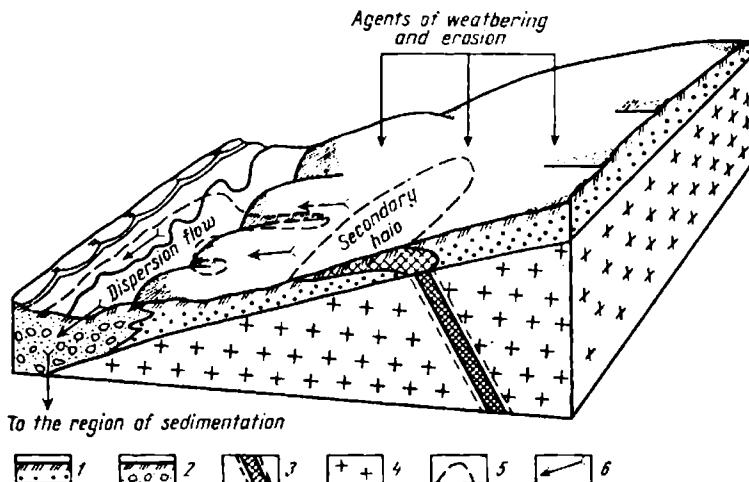
FIG. 5. Block diagram of a supergene dispersion field:
1—eluvio-deluvium; 2—alluvium; 3—orebody and its primary halo; 4—enclosing rocks; 5—contour of anomalous ore element contents in products of weathering, river water and vegetation; 6—direction of runoff

less than the general content of these metals in ores, respectively. Geochemical prospecting for oil employs methane determinations in the soil air starting from 10^{-5} %. After a detailed evaluation of a discovered geochemical anomaly shown to be promising, test pits are excavated or boreholes are drilled with the purpose of pinpointing the primary ore occurrence and estimating its importance.

Sec. 1.4. Geochemical Surveys

The studies of a geochemical field to find mineral deposits use methods of geochemical surveys. These basically consist in systematic measurements of the chemical element content along specified profiles or traverses. A system of such straight, broken or curved profiles of geochemical prospecting distributed over an area or directed to some depth forms a geochemical reconnaissance plot. Geochemical anomalies thus discovered are considered as targets of ore finding that should be evaluated. Depending on the medium to be sampled and tested methods of prospecting and surveys fall into

lithochemical, hydrochemical, atmochemical (gaseous) and bio-geochemical. A lithochemical survey concerns rocks found at the surface, in mine workings or boreholes as well as products of recent or ancient weathering of rocks and soils. A hydrochemical survey is a study of surface and subsurface waters. Atmochemical prospecting generally relies on studies of the earth air, sometimes of the near-surface air. Reconnaissance biogeochemical surveys are generally concerned with determinations of the chemical composition of indicator vegetation.

There may be terrestrial (pedestrian and automobile), aerial (airplane and helicopter) and underground surveys. Underground surveys fall into horizon-after-horizon lithochemical surveys in mines, borehole lithochemical tests of cores, geochemical logging of borehole walls and deep geochemical surveys of specified areas at a constant distance from the ground (more than 3 m) or at a level of a constant geological horizon by collecting samples or by lowering special transducers. Similar areal or profile surveys to a depth up to 3 m are generally termed ground or terrestrial surveys. Prospecting work may be conducted by surface water or underwater surveys studying fluvial, lacustrine or marine sediments and waters, plants or living organisms. Prospecting may rely on the measurements of the atmospheric dust, snow or gaseous metalloorganic compounds. These geochemical studies all differ very much in their practical importance for prospecting. It is the lithochemical method of prospecting for mineral deposits, primarily, ore deposits, that has proved particularly useful. All kinds of lithochemical surveys are constantly being executed in all mineralization areas. Less popular is geochemical prospecting for fossil fuel, particularly, petroleum and natural gas (cf. Sec. 6.3). Some methods, for example, atmochemical prospecting, have been extensively developing in the last few years; others, like biogeochemical prospecting, have for decades remained at an early stage of development or they have just begun to be developed (such as underwater surveys on the shelf, aerosol surveys, etc.). Some have begun to emerge only recently and their large-scale application would be premature. The main emphasis in the present book has been placed on methods of lithochemical prospecting for ore deposits, although general principles underlying these methods are of general value.

As has already been pointed out, geochemical surveys may or may not use sampling and rely on point discrete or continuous determinations of the chemical element values along profiles. In a geochemical survey that involves sampling the number of chemical elements determined in the samples collected is the greatest the larger the area being surveyed, the smaller the scale of the survey and the less known are geological features of the region in question. Sampling in a lithochemical reconnaissance survey makes it possible

to determine the contents of 35-40, sometimes 50-55 chemical elements. No contact or remote methods are currently available, such as would enable us to do away with sampling and make determinations of many elements with a sensitivity satisfying the requirements of a reconnaissance geochemical survey. Geochemical surveys without sampling are generally carried out when searching for a single chemical element, e.g., Be, B, F or Hg, less often for determining the total amount of several ore-forming elements (say, by the use of a "Poisk" device). Gamma-spectroscopic pedestrian, automobile and, particularly, aerial geochemical surveys for concurrent determinations of U (from Ra), Th and K (from the radioactive isotope ^{40}K) have proved especially popular and efficient.

Depending on the purpose in mind, we divide geochemical surveys into: (a) orientation surveys on a scale 1:1 000 000 or a smaller scale; (b) prospecting surveys to be successively conducted over the entire mineralization area on a scale 1:200 000, then 1:50 000; (c) detailed surveys of selected areas on a scale 1:10 000; (d) exploration surveys on a scale 1:1 000 and larger scales to be conducted within the boundaries of ore field of economic deposits being explored and exploited. The principle of proceeding from the general to the part, i.e. from small-scale to detailed geochemical surveys is in accord with the stages of geological prospecting adopted in the USSR.

To refer a geochemical survey to a definite scale, observation (sampling) points should be spaced so that at least one point be available per 1 cm^2 of the resultant geochemical map. Since square survey grids are seldom used and are warned against for practical purposes, an interval along a profile Δx will always be less than the distance between profiles $2l$. In the long run the scale of a survey is governed by the intervals between profiles, which, whatever the spacing of testing along a profile, should correspond to 1 cm of the scale of the final map. These requirements are to be invariably met by all types of litho-, hydro-, atmo- and biogeochemical surveys including ones that involve continuous measurements, so as to rule out any ambiguity [17]. The prospectors, however, are free to perfect procedures of geochemical exploration so that the purpose in mind could be attained by conducting surveys on smaller scales (or at larger intervals between observation points) than has been done previously.

Each method of geochemical prospecting has its own benefits and preferred scales permitting a better efficiency. The adequate choice of the procedure and scale will render geological work effective. Any type of geochemical exploration should be conducted along such lines as to unambiguously determine whether *genuine ore occurrences exist* in a given locality. Geochemical methods of determining potential mineralization areas are done away with for experience has shown that it is possible to appraise the potential mineral-

ization of a region from the inspection of sheets of the state produced 1:1 000 000 geological map by using principles of metallogenic analyses. Not a single portion of the globe's territory has remained not covered by geological maps. The ultimate goal of orientation geochemical surveys should invariably be the discovery of genuine ore-bearing belts with a numerical evaluation of the probable reserves of the metal of interest to us (see pp. 60-62).

Sec. 1.5. Parameters of a Geochemical Field

It will serve no purpose to try to identify the particular factors responsible for variations of the background values of an element at each sampling point from its average value. Analyses of background within a homogeneous area should be executed by the calculation of the frequency of the occurrence of different contents of the element in question. Leaving apart the causes of background variations at each particular point of a geochemical field, we consider these content values to be random variables the characteristics of which are provided by the estimated parameters of their statistical distribution. Such analyses have established that statistical distributions of background values are approximated by the normal distribution which is very important in many scientific disciplines. The fact that this principle finds wide use in nature and engineering may be explained in terms of A.M. Lyapunov's Central Limit Theorem (1900) which states that the normal distribution shows itself under conditions where the variation of the observed variables x is governed by commeasurable and independent effects of a number of different factors. It is this joint effect of diverse geological, geochemical, bioclimatic, technological and many other causes that governs the background content values of elements in rocks, soils, waters and other natural media. The normal distribution function is expressed by this relationship:

$$y = \varphi(x) = \frac{1}{s\sqrt{2\pi}} e^{-\frac{(x-\bar{x})^2}{2s^2}} \tag{3}$$

where $\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$ is the arithmetical mean of x which in the limit, given $N \to \infty$, tends to its mathematical expectation; $s =$

$$= \sqrt{\frac{\sum_{i=1}^{N}(x_i-\bar{x})^2}{N-1}}$$ is the standard deviation of random values

of x from $\bar{x}$; s^2 is the variance of x.

The normal distribution, Eq. (3), may be approximately satisfied by frequency distributions $y = \frac{n_i}{N}$ of the element content in samples

collected where n_i is the number of samples with the content $C_{i-1} \leqslant$ $\leqslant x \geqslant C_{i+1}$ in per cent. In other cases Eq. (3) is obeyed by frequency distributions of logs of element contents and assumes the meaning of a lognormal distribution according to which $x = \log C_i$. It was shown by N.K. Razumovsky in 1939 that the lognormal distribution generally holds for the frequencies of various content values of ore-forming elements in ores and rocks, of sizes of gold grains in placer deposits and of many other geological index characteristics. Distributions of major elements contents in rocks roughly conform to normal distribution. Although chemical elements distributions to be actually observed may differ from the normal or lognormal distribution, homogeneous geological assemblages mostly demonstrate a satisfactory agreement with these laws. The parameters $\bar{x}$ and s adequately characterize distributions that conform to the normal distribution which is well studied, so the fact that natural distributions are closely approaching this law is extensively used in geochemical exploration. However, the normal distribution of the element contents or their logarithms taken as a basis is only a convenient approximation, i.e. a rough description of the observed regularities. The normal distribution permits a definite frequency $y > 0$ of the occurrence of samples with *a negative element content* which is absurd. The lognormal distribution is free from this disadvantage. Yet, similarly to the normal distribution, it allows samples the element content in excess of 100 % which is as meaningless. That is why none of these relationships can be regarded as a theoretical law distributions of element contents in natural assemblages conform to. Rather, these laws may be assumed to be convenient for practical purposes.

The normal distribution curve has a bell-shaped configuration with a single peak at a point $\bar{x}$ and is symmetrical about the straight line $x = \bar{x}$. For the normal distribution the value of $\bar{x}$ corresponds to the most commonly occurring value of the random variable x or its mode and, owing to the symmetry of the distribution, coincides with its median, a value corresponding to the midpoint of an arranged series, i.e. dividing the entire data population in two. The equality of the arithmetic mean, mode and median is the most important characteristic of the normal distribution. This makes it possible to extend the previously formulated definition of geochemical background C_0 whose value corresponds concurrently to the average, most frequently occurring (modal) and median element content in a homogeneous area. Note that half of all points in the background area manifest the element content $C_x \leqslant C_0$, and the other half the element content $C_x \geqslant C_0$. The calculated theoretical values of the normal distribution function for $\bar{x} = 0$ and $s = 1.0$ can be found in all mathematical handbooks and texts on probability theory and mathem-

atical statistics. These latter also tabulate values of the integral function

$$\Phi(x_a) = \int\limits_{-x_a}^{x_a} \varphi(x)\, dx = \frac{2}{\sqrt{2\pi}} \int\limits_{0}^{x_a} e^{-\frac{x^2}{2}}\, dx \qquad (4)$$

characterizing the probability of that a random variable x, if it conforms to the normal distribution, will not exceed in absolute value the specified value of x_a. Tabular values of the probability integral $\Phi(x)$ represent dual criteria whereas in practical prospecting work it is positive geochemical anomalies, i.e. element contents exceeding C_0 that are generally important. The probability of that the random variable x will not be greater than the corresponding upper limit will be $0.5 + 1/2\Phi(x_a)$. Some values of these probabilities are listed in Table 3 simultaneously showing a probability of an opposite event, i.e. of that the value of x may inadvertently exceed the specified limiting value of x_a.

TABLE 3

Normal Distribution of x

Upper limit of x_a	Probability of x not exceeding x_a, %	Probability of opposite event, %	Upper limit of x_a	Probability of x not exceeding x_a, %	Probability of opposite event, %
$\bar{x}+s$	84.13	15.87	$\bar{x}+3s$	99.86	0.14
$\bar{x}+2s$	97.72	2.28	$\bar{x}+4s$	99.997	0.003
$\bar{x}+2.33s$	99.0	1.0			

Extending these data to the regularity of random background variations, we can select some threshold value $C_A > C_0$ above which fluctuations of the background effect will be of significance in terms of a geochemical anomaly thus suggesting possible ore. The probability of random background variations being found among them will be governed by the choice of the value of $t > 0$ determining the upper limit of such fluctuations

$$x_a = x + ts \qquad (5)$$

and the lower anomalous element content C_A. In each particular case the determination of C_A requires the estimation of numerical values of the local background parameters $\bar{x}$ and s. Depending on whether the normal or lognormal distribution is approximating the statistic distribution of background values, the values of $\bar{x}$ and s will be expressed in per cent (mg/l, g/t etc.) or in logarithmic units.

The choice of the value of t cannot be rigorously substantiated. If we adopt C_A at the level of $t = 4.0$, the probability of erroneously referring background variations to a class of geochemical anomalies will be negligible (see Table 3).

This, however, will cause a fraction of weak anomalies differing only in a minor way from C_0 to be lost. These anomalies may be of importance, in particular, when prospecting for deposits in deep-seated conditions. If we adopt C_A at a level of $t = 1.0$, weak anomalies will be detected to be later analysed. Yet, in so doing, another 15.87% of all background values will be erroneously referred to their number. During geochemical explorations, the total number of such spurious anomalies conditioned only by random variations in background may run into several thousands. It is not feasible to perform a geological survey, detailed prospecting and control of such a number of anomalies, and since we are unable to disregard the few ore-bearing anomalies that may enter this number, the geochemical survey will prove useless.

Element content determinations in samples employ extensive use of spectroscopy within errors conforming to the lognormality. The latter law is also obeyed by random error distributions in many other methods of prompt analysis under conditions of large spread of element contents in the collected samples. Errors of analysis enter as a term s_{tech} into the standard deviation of the background s. According to the theorem of addition of variances:

$$s = \sqrt{s_{nat}^2 + s_{tech}^2} \qquad (6)$$

Since s_{tech} has the meaning of a logarithmic quantity, statistic distributions of trace element contents during spectroscopic analysis of samples should be approximated by the lognormal distribution. The fact that negative and zero element content values inconsistent with Vernadsky's law are impossible is one of the advantages of lognormality. Accordingly, Eq. (5) assumes the role of a relationship between the logarithmic quantities: $x_a = \log C_A = \log \widetilde{C}_i + t s_{log}$. Clearing the logarithms we have:

$$C_A = \widetilde{C}_x e^t \qquad (7)$$

where $\widetilde{C}_x = C_0$ is the geometrical mean of the element content within the background area

$$\widetilde{C}_x = \text{antlog} \left(\frac{1}{N} \sum_{i=1}^{N} \log C_i \right) *$$

---

* Here and elsewhere a horizontal bar over a letter denotes the arithmetic mean, a curved bar the geometric mean.

[The quantity $\varepsilon = $ antlog $s_{\log}$ is generally called "*a standard factor*". In view of the above considerations as to the selection of the value of t, the lowest anomalous content, when trying to detect weak anomalies determined from one sampling point, in geochemical prospecting is taken equal to:

$$C_{A1} \geqslant C_0 \varepsilon^3 \qquad (8)$$

This relationship corresponds to a "three standard deviation" criterion ($+3\ s_{\log}$) extensively used in many engineering disciplines to determine quantities falling outside the probable values of a random normally distributed quantity. So that weak anomalies formed by a sequence of adjacent sampling points with increased pathfinder element contents below C_{A1} can be detected, it is usual to lower the threshold value according to the criterion

$$C_{A,\ m} \geqslant C_0 \varepsilon^{3/\sqrt{m}} \qquad (9)$$

where $m = 2, 3, 4, \ldots, 9$ is the number of points that may be joined, such as to show a common anomaly on the geochemical map.

It is rightfully assumed in the particular case that the increased element contents $C_x > C_0 \varepsilon$ induced by random background fluctuations will be distributed within the area in a uniform random fashion as separate points. By contrast, even weak but genuine anomalies will tend to approach structures responsible for the distribution of minerals regularly found at adjacent traverses forming groups of correlated points with common contours. The progressive drop in C_A is limited by the value of $C_0 \varepsilon$ whatever the values of $m \not> 9$, since

the probability of appearing increased contents, as $\tilde{C}_x$ is being approached, tends to 50%, and the index of geological correlation of contents $C_x > C_0$ is no longer unambiguous. The number of the established spurious anomalies in excess of their probable number 0.14% as determined by the criterion ε^3 (see Table 3) increases only insignificantly. Estimates of statistic parameters of background $C_0 \varepsilon$ and determinations of the lowest anomalous values of $C_{A1} - C_{A,\ m}$ use computers or conventional techniques from randomization samplings of limited magnitude, generally by plotting graphs of the cumulative frequency of various background values using probability grids [34] or microcalculators. Determinations are being made for each element or their appropriately selected population for homogeneous areas of the geochemical field. When the entirety of the available data is being handled using a computer, concepts as to stepwise-constant background are substituted by an approximation of background by a curved trend surface which is closer to the nature of the geochemical field.

Knowledge of the local background parameters permits one better to locate anomalies, their effective size and contrast. A geochemical

anomaly is understood to be a closed volume V where the numerical values of the geochemical field are at all points equal to or more than the specified magnitude of C_A. In a two-dimensional space the geo-chemical anomaly is bounded by a closed contour S in area; viewed in a cross section, it displays a width $2a$. Quite clearly, the size and shape of anomaly is governed by the particular minimum element content C_A at which the contouring is carried out. For example, during lithochemical surveys in Central Kazakhstan made in 1948-1953, copper was found in samples starting from 0.04% (sometimes even from 0.07%), although the true limiting sensitivity of analyses could even then be taken as 0.0001% for Cu. Under such conditions the effective, or observed, width of the geochemical anomaly shown in Fig. 6 was estimated to be 27 m from the results of a detailed exploratory survey with sampling points spaced at intervals 10 m. The same anomaly assessed as $C_A = = 2 \times 10^{-2}\%$ would have had an effective width $2a = 40$ m; and for $C_A = 1 \times 10^{-2}\% - 2a = = 60$ m. A further drop in the value of C_A to $8 \times 10^{-3}\%$ would have caused us to estimate the effective width as being 68 m etc.
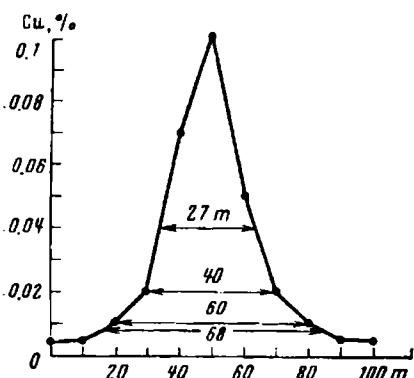

FIG. 6. Plot of variation of the effective (observed) width of a geo-chemical anomaly depending on the sensitivity of sample analysis and choice of the lowest anomalous copper content

None of these linear values can be regarded as a parameter to any degree approximating the actual anomaly size which defies rigorous determinations.

A geochemical anomaly can be pinpointed provided even a single sampling point should fall within its contour. That is why the geometrical dimensions of an anomaly should be determined within the limits of $C_x \geqslant C_{A1} = C_0 e^3$. The magnitude of the standard factor ε, by virtue of Eq. (6), is governed by the accuracy of the survey whose increase, owing to the diminished term s^2_{tech} causes a drop in the value of e^3, and, consequently, C_A, thus enlarging the dimensions of the anomaly. On their periphery geochemical anomalies are asymptotically approaching the local background, so their size cannot be exactly determined and it is liable to repeatedly vary depending on the errors incurred in the survey. That is why we may speak only of the "effective" or observed size of a geochemical anomaly which does not characterize the chemical elements but is of much technical importance. It would be wrong to try to establish the

"true" size of an anomaly. We can contour an anomaly, even given other, lower extreme levels of $C_{A,m}$ in the interval to $C_{A_9} = C_0 \varepsilon$ at $m \geqslant 9$. The choice of inner anomaly contours multiple to the standard deviation of $C_0 + ts$ (or $C_0 \varepsilon^t$) at values of $t \gg 3$ is unreasonable both in mathematical and geochemical terms. High inner contours ("isoconcentration contours") and maximum contents C_{max} in obvious anomalies should be expressed in per cent, g/t or other common units.

The contrast index which is often confused with the C_{max}/C_0 ratio is, similarly to size, a characteristic of an anomaly. To correctly evaluate this important characteristic requires a comparison of the anomaly not only with background but also with its stability the measure of which is the standard deviation s (or ε). Should the local background remain absolutely homogeneous throughout all points ($s = 0$, $\varepsilon = 1.0$) it would pose no problem to detect whatever weak anomaly, given whatever high background. That is why the contrast index of a weak anomaly γ is provided by a signal-to-noise ratio. The definition, borrowed from radio engineering and abbreviated as S/N or SNR, has been extensively used in science to designate weak indications as detected among noise signals. In our particular case the desired signal is the amplitude of the geochemical anomaly C_{max} minus background, and the noise is the magnitude of the standard deviation of background. Consequently,

$$\gamma = \frac{x_{max} - x_0}{s} \qquad (10)$$

or, taking into account the lognormal distribution of the trace element contents,

$$\gamma = \frac{\log C_{max} - \log C_0}{s_{\log}} = \frac{1}{\log e} \times \log \frac{C_{max}}{C_0} \qquad (11)$$

Figure 7 provides an example of the comparison of contrasts of two weak anomalies with identical values above the background $C_{max} - C_0 = 20$ for different parameters of the geochemical background.

Equation (11) is principal for an appraisal of contrast of a weak geochemical anomaly when comparing the effectiveness of various geochemical methods to reveal it. For values of $\gamma \geqslant 3$ the anomaly is liable to be revealed from even a single observation point; given $1 \leqslant \gamma < 3$, for the anomaly to be discovered, it is necessary that within contour of the anomaly $C_{A,m}$ points should fall, where $m = 2, 3 \ldots 9$; for $\gamma < 1$, by virtue of Eq. (9), no anomaly above the lode may be detected. This does not mean that no anomaly exists, rather, one would have to resort to special methods of mathematical handling of the available data, or refer to alternative methods of investigation of the geochemical field, such as will increase the SNR.

The calculation of the contrast characteristic (11) is reasonable only for weak anomalies. The amplitude of an obvious anomaly will be shown by the absolute value of C_{max}.

The assessment of parameters of the local geochemical background is a prerequisite to reliably detect anomalies, correlate their effective dimensions, determine the contrast characteristics of weak anomalies and compare the practicability of the different methods and techniques of investigating the geochemical field. On the other hand, statistical analysis of background areas of the geochemical field is
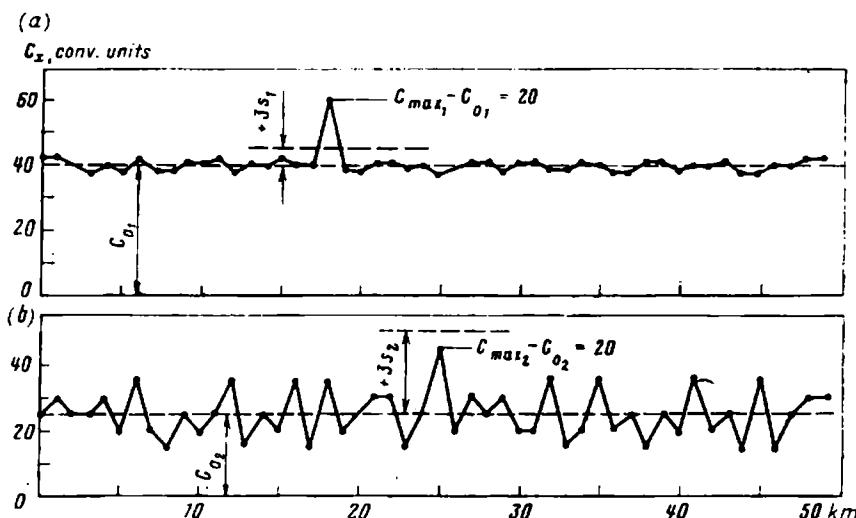

FIG. 7. Comparison of contrast of two weak anomalies for different background parameters:

$a - C_{01} = 40$; $S = 1.5$; $C_{A_1} = 45$; $\gamma \gg 3$ and $b - C_{02} = 25$; $S_2 = 7.6$; $C_{A_2} = 50$; $\gamma < 3$

a necessary but only initial condition for a quantitative analysis of the geochemical evidence. Geological results of exploration determine analysis not of the background, but of anomalous areas of the field. In geochemical anomaly zones the element contents exhibit a spatial-ordered (determined) pattern where methods of mathematical statistics do not apply or have limited applications.

Statistical estimates of the mean and variance of any variables are sensible only on the condition that these data are homogeneous. Only in this case can sampling adequately mirror the general population of the data and the increased number of the data obtained enhance the accuracy of the estimates. The fact that the same statistical estimates are not valid, unless the homogeneity condition is satisfied, is illustrated by simple examples (Fig. 8) that can be referred to the results of any geochemical field tests.

The results of analyses of n_1 samples collected within a homogeneous granite massif, away from its endocontact zone, may enable one to find estimates of the mean $\bar{C}_1$ and standard deviation s_1 of the contents of any chemical element. If we continue field tests without leaving the contour of the rock mass, collecting another n_2 samples, then the estimates of $\bar{C}_2$, s_2 from $n_1 + n_2$ samples will verify the previously obtained data not changing these latter appreciably. Both the first and the second estimates are objective characteristics of these granites; their numerical values, as the number of samples collected is increased, converge in probability to their true value (taking into account the particular method of field testing and the accuracy of analysis). Should the sampling profile intersect the contact zone getting to effusive host rocks with a different content of the element being determined, then the estimates of $\bar{C}_3$ and s_3 from n_3 samples or from the population of $n_1 + n_2 + n_3$ samples will have no stable geochemical meaning, being entirely governed by the random ratios of samples collected from the granite and effusive materials (see Fig. 8a). Such samplings obtained through *a mixture* of nonuniform populations of data cannot be used for statistical treatment. To estimate the mean and standard deviations of element contents from the results of testing of two different rock species, it is necessary that the initial data be preliminarily grouped into homogeneous populations.

Nonuniform data for which estimates of statistical parameters of distribution have no stable meaning are illustrated by ore element contents in anomalies. Any estimates of the mean and standard deviation of the metal content in a geochemical anomaly zone (see Fig. 8b) from n_4, n_5 or n_6 samples randomly change their values depending on the arbitrarily chosen limits of calculation. The same is true of analysis of the statistical distribution of the metal content in the orebody and wall rocks from the data of a geochemical testing of a core from an exploratory borehole (see Fig. 8c). It will be recalled that the boundaries of a geochemical anomaly cannot be rigorously determined. For this reason any estimates of $\bar{C}_7$ and s_7 for anomalies discovered from n_7 (or n_4) samples would be conditioned by the choice of C_A and cannot be regarded as being natural characteristics of the object of study. This does not rule out the existence of conditions under which the estimates of the mean content and variance of the metal content in the metalliferous zone can be regarded as objective quantities. An example of this kind is shown in Fig. 8d for the case of a deposit of an appreciable thickness (e.g. a stockwork deposit) in the central portion of which one can observe "random" variations of the metal content about some constant level. In this case in the sampling interval of n_8, away from the boundary of the orebody, the metal contents in the samples manifest a homogeneous data popu-
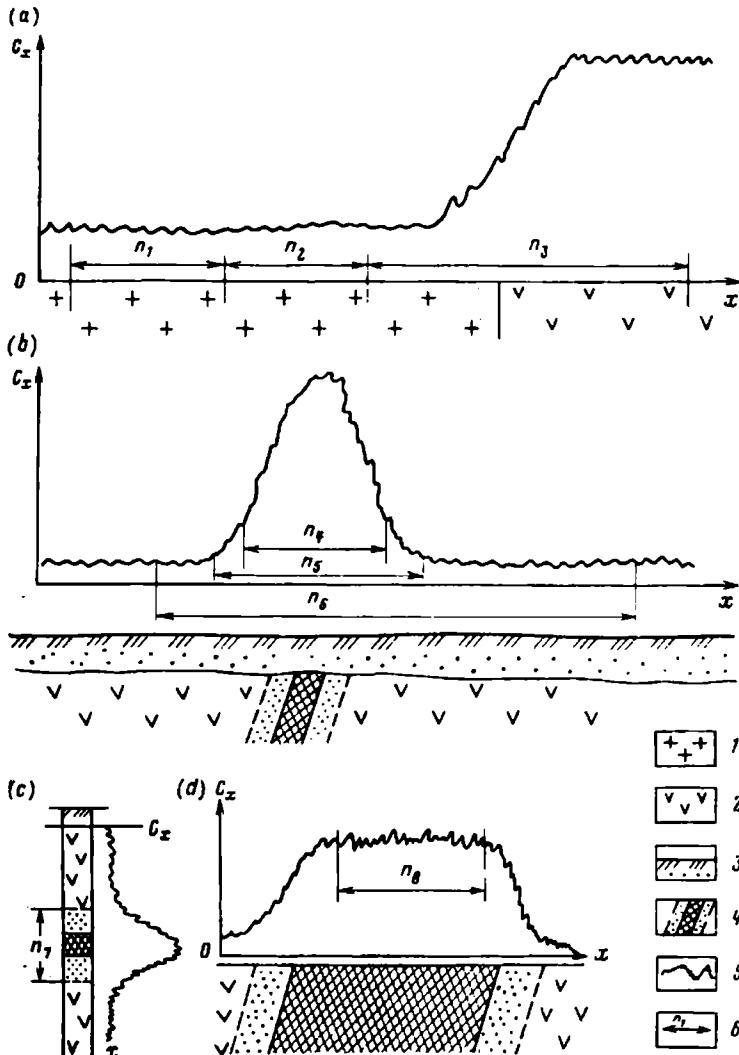
FIG. 8. Plots of homogeneous "random" (samples n_1, n_2, n_8) and nonhomogeneous spatially ordered (samples n_3-n_7) ore element contents:

a — in granites (1) and principal effusive rocks (2); b — in eluvio-deluvium (3); c — in core from borehole; d — in stockwork; 4 — orebody and its primary halo; 5 — ore element content plots; 6 — geochemical testing intervals

lation, and statistical parameters $\bar{C}_8$, s_8 will consistently characterize this and similar mineralization intervals.

Estimates of average contents and variance as consistent quantities may as well be found for a sequence of various rocks or different other natural formations grouped together for one or another purpose in mind. Conditions for this are a plurality of populations to be grouped (e.g. rock species, landscape types) and minor dimensions of individual nonuniformities compared with the size of the object under study which ensures the representability of the sampling data. An example can be provided by clarkes of the geospheres whose values undoubtedly are important in statistical and geochemical terms.

Analysis of spatial ordered determined distributions of element contents in a geochemical anomaly uses a body of principal equations of mathematical physics. It is the purpose of this analysis to establish causality between the element contents and space coordinates, duration of processes, parameters of the geological setting and properties of the chemical element. Such relationships responsible for the occurrence of geochemical anomalies in the different geospheres are found by considering simplified idealized models of the process. These relationships may partially be established by borrowing solutions from the domain of differential equations of heat and mass transfer, diffusion, material balance, kinetics of chemical reactions or hydrodynamics. The obtained physicomathematical relationships, Eqs. (1) to (2), are necessary for quantitative analysis of the discovered geochemical anomalies, taking into account departures from an idealized picture that are inevitable under actual conditions. Clearly, it is not feasible or reasonable to work out a mathematical theory of the occurrence of geochemical anomalies for each individual chemical element. That is why, when establishing general regularities of the formation of the anomalous geochemical field, we study the behaviour of some hypothetical element or metal. Individual properties of the chemical elements are allowed for by the numerical values of coefficients entering into the determined functional relationships.

For a series of numerical values that characterize anomalous fields of the same type a need arises to estimate their average values and confidence levels, variances and correlation interrelations. Thus, apart from mathematical procedures for analysis of anomalous fields based on determined models we use we should assess the results obtained in terms of probability statistics. The differentiation of prospecting geochemistry problems into two classes solved by referring to determined and probability statistic models is, to a certain extent, arbitrary. Any natural "random" distributions are not without cause. There are no ordered distributions in nature, such as would not involve a random component. However, we can

draw a distinct line between these types of problems and techniques of mathematical analysis of the geochemical fields. Viewed in this context, concepts of *parametric and non-parametric* geochemical index characteristics are essential.

Geochemical parameters are understood to be variables with an objective meaning the numerical values of which are defined more exactly concurrently with increasing the accuracy of a study. Such are, e.g. the average lead content in a homogeneous rock whose value is determined more accurately as the number of samples collected increases and more accurate methods of their analysis are employed. By contrast, numerical values of non-parametric characteristics defy rigorous determination, they *arbitrarily change* with enhancing the accuracy of investigations or *are known in advance.* Examples of typical non-parametric characteristics are the "occurrence" of the chemical elements which, according to Vernadsky's law, will be equal to 100%, or the dimensions of geochemical anomalies (see Fig. 4). Non-parametric characteristics include estimates of the average element content in a geochemical anomaly (see Fig. 8), the extent of any geochemical anomaly in a drainage system due to their asymptotic approximation to the background or proximity of the final runoff reservoir etc. Some non-parametric index characteristics are of much engineering importance, such as, e.g. the average metal content in an orebody (governed by the arbitrarily chosen border tenor) or the effective dimensions of a geochemical anomaly as referred to the lowest anomalous content limit. However, the numerical values of non-parametric characteristics do not illustrate natural properties of an object of study. It is impermissible to compare them with the element atomic masses, valencies, ion radii, ion potentials, solubilities of compounds or other objective characteristics of a material or to range ore elements according to the values of non-parametric characteristics. These latter cannot be relied upon when it is desired to substantiate some theoretical or consistent methodological conclusions.

It is sometimes easy to pass from non-parametric index characteristics to the geochemical parameters which are invariably preferable for the description of the geochemical field. For example, the average ore element content in an anomaly and the width of the latter in a profile are non-parametric quantities. The former of these, minus the background, vanishes in the limit, the latter tends to infinity, or:

$$\lim (\bar{C}_A - C_0) \rightarrow 0; \quad \lim 2a \rightarrow \infty \qquad (12)$$

However, any product of these interrelated and fairly indeterminate quantities gives rise to a quite stable parametric index characteristic illustrating *the amount of metal* (in meter percent) in the

particular cross section of the anomaly, or

$$2a\,(\bar{C}_A - C_0) = M \tag{13}$$

The value of this objective geochemical characteristic called the linear productivity of an anomaly, even if given lowest computation standards, can be determined fairly accurately, the degree of accuracy increasing in direct proportion to the increase of detail of the study and precision of sample analysis. A very important parametric meaning for characteristic of a geochemical anomaly is provided by the areal productivity

$$P = S\,(\bar{C}_A - C_0) \tag{14}$$

This quantity characterizes the amount of the chemical element (in $m^2\%$) in excess of the background value contained within the contour of the anomaly as projected on a plane and provides a criterion to compare the anomalies. Similarly to the parameter M, it is independent of arbitrary decisions. The amount of the chemical element Q in tonnes, in excess of the background value, as contained within the volume of the particular anomaly also represents a geochemical parameter. A remarkable property of the linear, areal and volume productivities of a geochemical anomaly is that they are independent of the scales of the geochemical surveys which yield the data they are computed from. It can be demonstrated by referring to an estimate of the parameter P for a definite area S_0 where, besides background values of the ore element, lithochemical anomalies of different size are developed. This area would be explored the most completely by continuous observations and with infinitesimal spacings between profiles ($\Delta x \to 0$; $2l \to 0$) and an infinitely large number of observations $N_0 \to \infty$ constituting a general population of data. In conformity with Eq. (14), for the true values of S_0 and C_0 the true value of P is determined by the mathematical expectation of $\bar{C}_x$. The value of P can be found with a specified degree of accuracy by determining $\bar{C}_x$ from random data selection with the number of observations $N < N_0$ which follows from the unbiased estimate of the mean. This, in fact, implies an extremely sparse survey net where N remains a representative population. On this condition estimates of P remain correct, whatever the scale of the survey, refining as the density of observations increases.

Linear and areal productivities of a geochemical anomaly, given a uniformly spaced observation grid, are generally calculated by referring to relationships similar to Eqs. (13) and (14)

$$M = \Delta x \left(\sum_{x=1}^{n} C_x - nC_0 \right) \tag{15}$$

$$P = \Delta x 2l \left(\sum_{x=1}^{N} C_x - NC_0 \right) \tag{16}$$

If the values of M_i are preliminarily estimated in each of m profiles across the anomaly, P is determined from this relationship

$$P = 2l \sum_{i=1}^{m} M_i \qquad (17)$$

The procedure is the same when P is to be estimated by continuous observations along a profile. In the latter case the values of linear productivities of anomalies are found as areas bounded by the plot of $C_x = f(x)$ and the line of local background. As can be seen from Eq. (16), in computations of P any, even the shortest in length, anomaly is nominally assigned a length $2l$ (and width Δx). Consequently, given that the length of an anomaly is $2b < 2l$, its productivity will be exaggerated by a factor of l/b. However, of the total number of all anomalies of such a length, surveys on the particular scale will reveal only a fraction proportional to the b/l, ratio, and computations of P will be correct. Proceeding along these lines for a case of $2a < < \Delta x$, we arrive at the conclusion, already made, as to the fact that computations of P are independent of the scale of the geochemical survey, whatever the relations between S and ΔS. Referred to a fairly large area, the estimate of P characterizes the total productivity both of the located anomalies and ones omitted by the survey which is an essential feature of this parameter. All that has been said about independence of the scale of the surveys holds good for computations of the above background value of chemical element amount in the volume of the particular anomaly or a fairly large three-dimensional segment of a geochemical field. The term "volume productivity" has not found use in geochemical prospecting, and the corresponding quantities are generally known as "geochemical reserves" of the element in question within the given volume, in particular, to a depth H m or for a layer of 1 m, expressed in tonnes and denoted by the symbols Q_H or q t/m. In definite circumstances one fraction of geochemical reserves or another may be assumed as prognostication estimates of resources of a mineral and then as quantities of economically important supplies of the particular material. Depending, as they do, on the chosen minimum economic metal content, economic supplies, unlike geochemical reserves, are non-parametric values.

Another important feature of index characteristics of the above-the-average value of an element in a geochemical anomalous area is the presence of proportionality relationships between these parameters for different groups of interconnected anomalies. So, e.g. over a wide range of geological conditions there exists a direct relationship between the productivity of a primary mineralization (M_p, m %, P_p m^2 %) and that of its secondary lithochemical dispersion aureole

(M, P) in the regolith, or

$$M = kM_p \qquad (18)$$

$$P = kP_p \qquad (19)$$

where $k \lessgtr 1.0$ is a local productivity coefficient.

No doubt, higher than average metal contents in a hydrochemical, biogeochemical, gaseous mercury and some other anomalies are, in turn, directly related to the productivities of secondary dispersion aureoles and primary mineralization. The straightforward relations (18) and (19) illustrate the basic concepts of exploration geochemistry, they largely govern the procedures of geochemical surveys and principles of geochemical data interpretation.

A multi-dimensional pattern is specific for the geochemical field, since the contents of a large number of chemical elements have to be concurrently determined in geochemical exploration. Accordingly, the characteristic of the field is augmented by data on the correlations between numerical ratios of the metal contents or their productivities. Each point of the geochemical field displays gradients along the axes of space coordinates and a direction in which it varies the most. Similarly to other physical fields, the geochemical field obeys the principle of superposition which means that the effects of two or more sources are summarized.

In descriptions of geochemical fields the notation of variables, numerical indices or of any other constants should use conventional letter symbols listed at the beginning of book.

Sec. 1.6. Targets of Search

As has been shown by experience gathered all over the world, only such deposits are of special economic importance that contain the bulk of the known reserves and mineralized regions being exploited. Small deposits may prove of practical value only if they are found close to operating mines and large explored deposits of the same mineral. Moreover, the discovery of one or more small deposits and individual orebodies, even if of appreciable local value, is unlikely to alter the raw material budget even in terms of a mining district. It would be possible to continuously increase the amount of reserves of economic importance only by discovering new large deposits. That is why for efficient prospecting it is necessary to take into account the proportion between the number of deposits of different size, to distinctly formulate the ultimate objective of the exploratory operations and to appraise the probability of discovering deposits of a specified size. The best way to tackle such problems is by referring to a decimal ranking classification of deposits according to economic reserves as proposed by V.I. Krasnikov which assumes

the adjacent size groups of the reserves as differing by an order of magnitude.

If we define the reserves of deposits in a group of minimum economic reserves as $n \times 10^m$ t, we will have for a medium-size deposit $n \times 10^{m+1}$ t, and for a mineralization area of noneconomic importance nominal reserves $n \times 10^{m-1}$ t. The reserves of a large deposit will amount to $n \times 10^{m+2}$ t, and those of a unique deposit $n \times \times 10^{m+3}$ t. The scale may be shifted and, depending on the availability of raw materials and their character, n may be assigned numerical values from 1 to 9; and m, values of any positive or negative integers which does not affect the conclusions that may be made. Good agreement between the decimal classification and current concepts of ranking of deposits is validated by the data in Table 4 which lists estimated deposits classified into three sizes.

TABLE 4

Decimal Classification of Deposits According to Reserve Values (After V. I. Krasnikov, with Alterations)

Materials	Reserves, t			n
	small	medium	large	
Iron ores	$n \times 10^7$	$n \times 10^8$	$n \times 10^9$	2-5
Bauxites, phosphorites	$n \times 10^6$	$n \times 10^7$	$n \times 10^8$	2-5
Manganese and chrome ores, fluorite	$n \times 10^5$	$n \times 10^6$	$n \times 10^7$	1-3
Copper, lead+zinc, nickel sulphide, niobium (Nb_2O_5)	$n \times 10^4$	$n \times 10^5$	$n \times 10^6$	1-5
Molybdenum, tungsten (WO_3), tin, antimony	$n \times 10^3$	$n \times 10^4$	$n \times 10^5$	1-3
Mercury, beryllium (BeO), cobalt, silver, uranium, bismuth	$n \times 10^2$	$n \times 10^3$	$n \times 10^4$	1-3
Rare and dispersed elements	$n \times 10^1$	$n \times 10^2$	$n \times 10^3$	1-9
Gold, platinum	$n \times 10^0$	$n \times 10$	$n \times 10^2$	1-5

According to V.A. Pervago, porphyry copper deposits may on the average be assumed as being a large one if its reserves amount to 3 million t, in the Far North these estimates run into 5 million t of Cu. The range of a size class of deposits may range from $1/3n$ to $3n$, where n is the mean value (more precisely, $0.316n$ to $3.16n$, since $\sqrt{10} = 3.16$). Porphyry copper deposits with reserves over 9 million t of Cu under conventional conditions and over 15 million t under conditions of the Far North may be considered as unique. There are only a few deposits in the world whose reserves are greater than unique by an order of magnitude. As proposed by E.M. Kvyat-

kovsky, such deposits should be described as phenomenal. These latter include the gold fields of the South African Witwatersrand, platinum deposits of the Bushveldt complex in Transvaal, bauxite deposits in Australia.

The numerical relationships between the discovered mineralizations of different reserve magnitudes fail to mirror the actual relationships, since the probabilities of discovering the deposits of various sizes are not the same. Other factors being equal, a large deposit is easier to pinpoint than a smaller one. A larger mineralization of identical ore quality will be greater in extent and depth. In the general case a large deposit will display more outcrops of the ore and vaster zones of altered rocks. So will more intense, larger in area, numerous geochemical and geophysical anomalies accompany major mineralization zones. Exploration traverses are more likely to strike a large deposit in a geological, geochemical or geophysical survey, whereas a smaller orebody may fall between them and thus remain undetected. In mathematical terms this relationship is expressed by a probability of striking a target of search by the specified prospecting net of traverses on the condition that at least one (two) observation point should fall within the contour of the target. When continuous observations are being made, then the probability Π of a randomly oriented linear object, $2b$ in length, given a traverse net with a spacing $2l$, with $b \leqslant l$, will be found by solving Buffon's problem (1777):

$$\Pi = \frac{2b}{\pi l} \qquad (20)$$

Deposits and orebodies of the same genetic type of different reserve magnitudes may be assumed to be similar geometric and geochemical bodies. Consequently, with identical ore grade values, linear dimensions of two similar deposits will be expressed by the following relationship:

$$L_1 : L_2 = \sqrt{\overline{Q_1}} : \sqrt{\overline{Q_2}}, \qquad (21)$$

and areal dimensions by

$$S_1 : S_2 = (\sqrt[3]{\overline{Q_1}})^2 : (\sqrt[3]{\overline{Q_2}})^2 \qquad (22)$$

The decimal ranking classification of deposits makes it possible, whatever the actual dimensions of a lode, to find ratios between linear and areal dimensions of small, medium and large deposits by referring to these relationships:

$$L_{sm} : L_{med} : L_{lar} = \sqrt[3]{1} : \sqrt[3]{10} : \sqrt{100} = 1 : 2.15 : 4.64 \qquad (23)$$

$$S_{sm} : S_{med} : S_{lar} = (\sqrt[3]{1})^2 : (\sqrt[3]{10})^2 : (\sqrt{100})^2 = 1 : 4.64 : 21.5 \qquad (24)$$

Figure 9 shows cross sections of three lens-shaped congruent bodies whose volumes and, consequently, run-of-mine ore reserves differ by a factor of 10 and 100. It is the L and S relationships that will mirror discovery probabilities of searches for deposits of different reserve magnitudes, even if the probabilities themselves may remain unknown. These relationships will hold until all small, medium and large deposits have been discovered which can take place only in a distant future. That is why the number of mineralizations as recorded in a cadastre should be re-evaluated by referring to the relationships between linear and areal dimensions of the congruent figures involved. It will be recalled that visual methods of prospecting for
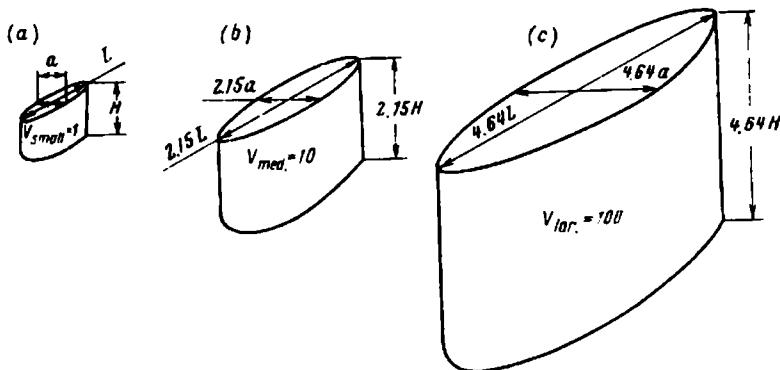

FIG. 9. Linear and areal dimensions of similar figures, given volume proportion $(a : b : c) : 1 : 10 : 100$:

$a - S_{sm} = 1$; $V_{sm} = 1$; $b - S_{med} = 4.64$, $V_{med} = 10$; $c - S_{lar} = 21.5$; $V_{lar} = 100$

mineral deposits relied in the past on the length (veins, extended lenses, beds), and the probability of the event obeyed Eq. (20). A calculation, in conformity with Eq. (23), discloses an approximate decrease of the number of adjacent reserve ranking classes toward larger magnitudes with a ratio 7:1. This has made it possible, in particular, to extrapolate the expected number of ore showings of noneconomical importance followed by ore manifestations not taken into account by the cadastre. When carrying out geochemical exploration generally aimed at discovery of anomalies of the main valuable component we must take into consideration additional "reserves" of the metal contained in the primary halo of the orebody. In the general case, increasing in absolute value for large deposits, the relative fraction of the metal in the primary halo drops with increasing the total reserves of the metal in the target of search and, clearly, will be increased to 100% in ore manifestations of noneconomic importance.

What has been said above permits generalization of the expected relationships between the characteristics of the different reserve ranking deposits as to the respective primary and secondary lithochemical anomalies (Table 5). This, in turn, will enable us to densify

TABLE 5

Relationships Between Deposits of Different Reserve Magnitudes [33]

Index characteristic	Reserve magnitude classes			Ore mani-festations
	large	medium	small	
By number in relation to a large deposit	1	7*	49	343
Same, %	0.25	1.75	12.25	85.75
By economic reserves in the deposit in relation to a small deposit	100	10	1	—
Same, in class, %	46	32	22	—
Geochemical "reserves" in the deposit in relation to a small deposit	49	7	1	0.143*
Areal characteristics of primary lithochemical anomalies in relation to a small deposit	13.4	3.66*	1	0.273*
Same, linear characteristics	3.66	1.91*	1	0.523*

Note. Asterisks show common ratios

the net of prospecting, such as to ensure, with a specified probability, the discovery of a mineralization of a given size should it occur within the area being explored.

In a search for mineral deposits from data on geochemical anomalies the calculation of a rectangular net for a geochemical survey is made by referring to approximate equations of A.M. Shurygin:

$$\Pi^{(1)} = 1 - e^{-S/\Delta S} \tag{25}$$

$$\Pi^{(2)} = 1 - e^{-S/\Delta S} (1 + S/\Delta S) \tag{26}$$

$$\Pi^{(i)} = 1 - e^{-S/\Delta S} \left[1 + (S/\Delta S) + 1/2\,(S/\Delta S)^2 + \ldots \right.$$

$$\left. \ldots + \frac{1}{(i-1)!}\,(S/\Delta S)^{(i-1)} \right] \tag{27}$$

where $\Pi^{(1)}$, $\Pi^{(2)}$, $\Pi^{(i)}$ are probabilities of finding within the contour of a mineralized area at least one, at least two or at least i points of a rectangular survey net*; S is the area of the zone being explored,

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* Eqs. (25)-(27) cannot be used for calculations of a net to search for deposits from their dispersion flows (cf. Sec. 2.4).

in the particular case, of a litho-, hydro-, atmo- or biogeochemical anomaly of any shape; ΔS is the unit area of a mesh of the survey net.

Table 5, taking into account Eq. (25), permits us to calculate the expected outcome of a lithochemical survey of an unlimited area with a "medium" mineralization. The proportionalities, Eqs. (18) and (19), make it possible to consider the relationships between the areal and linear characteristics of deposits of different reserve value listed in the lower lines of Table 5 as being true for the effective
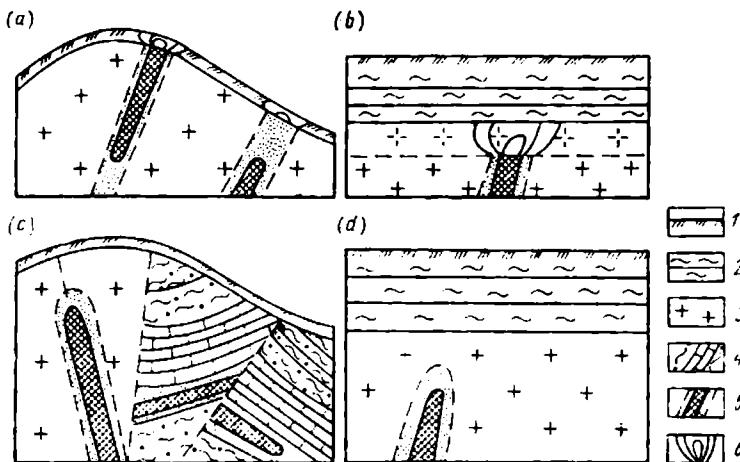

FIG. 10. Ore deposits under different conditions of occurrence:
a — outcropping; b — concealed; c — blind; d — blind;concealed. 1 — today's eluvio-deluvium; 2 — allochthonous deposits; 3, 4 — enclosing rocks; 5 — orebodies and their primary halos (associated with the principal ore element); 6 — secondary residual dispersion aureoles

dimensions of secondary residual dispersion aureoles. If we select a survey net proceeding from a probability of discovery of large deposits $\Pi_{lar}^{(1)} = 0.99$ which corresponds to a case $S_{lar}/\Delta S = 4.61$, we have $\Pi_{med}^{(1)} = 0.715$ and $\Pi_{sm}^{(1)} = 0.291$. Consequently, these surveys, if conducted over a large area, are likely to discover some 75 % of the total metal reserves concentrated in deposits cropping out at the erosional surface.

What has been said about the relative numbers of deposits of different ranking and the expected results of prospecting operations should be regarded as generalizations and in each particular case important departures from these may occur. The generalized patterns primarily are typical of orebodies found at the horizons of today's eroded occurrences. It is these outcrops (Fig. 10a) for all metals, excepting Fe, that still contain the bulk of economically important reserves. In mineralization areas of the eastern and, notably, north-

eastern Soviet Union as well as in the developing countries of Asia, Africa and Latin America, one may well expect outcrops of such mineralizations. As these mineralization areas fairly easily detected by geochemical exploration are being exhausted, we are liable to switch gradually to prospecting for deposits occurring in more involved conditions of occurrence, e.g. blind orebodies with supraore primary halos coming to the earth's surface (see Fig. 10a). This is the case of the traditional mineralization areas of the USSR and most developed nations in Western Europe and USA. That is the reason why geochemical prospecting, apart from exposed occur- rences, hunts also for suboutcrops, i.e. *buried deposits* previously coming to the surficial horizons but later overlain by overburden of recent origin and of minor thickness (see Fig. 10b). The most impor- tant potentialities are hidden in blind (or concealed) orebodies as well as endogenic and exogenic deposits under conditions of blind occurrence of primary halos of the principal ore-forming element (see Fig. 10c). Primary halos of pathfinder elements, secondary salt, gaseous and biogeochemical dispersion aureoles related to these deposits may reach the ground surface thus permitting detection by the use of special techniques of geochemical exploration. A still further objective seems to be directing exploration efforts toward concealed deposits at greater depths (see Fig. 10d). By assuming in advance the diversified modes of occurrence of economic deposits, the methodology of geochemical surveys takes an individual approach to the appraisal of each particular discovered anomaly the total number of which may sometimes run into several hundred. The shapes and actual dimensions of identically ranked deposits will naturally vary from one deposit to another depending on its genetic type and the material involved. Other conditions being equal, however, due to common economic criteria, whatever the valuable material in hand, the costs of winning 1 m^3 of ore will be the same, whether the ore content be 65% of Fe, 0.8% of Cu or 4×10^{-4}% of Au. This levels down the requirements put by the industry on rock mass volumes in deposits of different metals, especially of higher ranking classes permitting opencast mining, the most advantageous method of extraction of ore which can be substantiated by comparing the data on four different deposits (Table 6). The values of their extractable reserves differ by a factor of 1.3 million, the content of the valuable component in ores differs by a factor of 50 000 (P_2O_5 : Au), yet they differ inappreciably in terms of rock mass volumes. The linear dimensions of similar figures are even less affected by these differ- ences. At the prospecting stage, this circumstance makes it possible to generalize the concept of ore deposits and rely on empirical data on the average effective dimensions of lithochemical anomalies suggesting large deposits of different valuable materials. Numerical ·characteristics of large deposits must be considered in temporal

geological and economic terms and cannot be thought as represent-
ing natural parameters. Ever growing requirements are being put
by the industry on reserves of mineral materials in deposits ranked
as large ones, concurrently lowering the standards to be met by
minable minerals. So, e.g. the average copper content in ores being
won has dropped almost tenfold during the last hundred years.

TABLE 6

Comparitive Characteristics of Large Deposits

Valuable component	Reserves, thousand tonnes	Valuable component content, %	Density, t/m³	Volume of rock mass, millions, m³	Ratios of linear dimensions for similar figures
Copper	3×10^3	0.8	2.65	141	1.22
Molybdenum	3×10^2	0.15	2.60	77	1.0
Phosphate ores (P₂O₅)	4×10^5	20	2.90	138	1.21
Gold	3×10^{-1}	4×10^{-4}	2.60	29	0.72

Notwithstanding the great difference in the estimated reserves of
the deposits currently ranked as large and the average content of the
valuable component in ores classed as "rich" or "common", special
investigations point to the relationship between these quantities
for various chemical elements and the patterns of their distribution
in the earth's crust. These problems have been given particular notice
by E.M. Kvyatkovsky who has established a series of relationships
between the global reserves, size of deposits, metal contents in ores

TABLE 7

Economic Reserves of Large Deposits and Clarke Values of the Lithosphere [34]

Chemical element	Reserves Q_{lar}, t	c_C, %	Chemical element	Reserves Q_{lar}, t	c_C, %
Fe	5×10^9 (ore)	4.65	Sb	3×10^5	5×10^{-5}
P	4×10^8 (20% P₂O₅)	0.093	W	3×10^5 (WO₃)	1.3×10^{-4}
F	2×10^7 (40% CaF₂)	0.066	Sn	2×10^5	2.5×10^{-4}
			Co	3×10^4	1.8×10^{-3}
			Be	3×10^4 (BeO)	3.8×10^{-4}
Cu	3×10^6	4.7×10^{-3}	Bi	2×10^4	2×10^{-5}
Zn	2×10^6	8.3×10^{-3}	Hg	2×10^4	8.3×10^{-6}
Pb	2×10^6	1.6×10^{-3}	Ag	1×10^4	7×10^{-6}
Ni	1×10^6	5.8×10^{-3}	Au	300	4.3×10^{-7}
Nb	1×10^6	2×10^{-3}			
Mo	3×10^5	1.1×10^{-4}			

and clarke values of chemical elements [18]. Convincing proof of the relation between geological and economic requirements and actual geochemical regularities is provided by a close correlation between the reserves of the useful material in deposits of the same size class and clarke values of the elements in the lithosphere (Table 7) characterized by a ranking correlation coefficient $r_{xy} = 0.873$ with $r_{s\%} = 0.468$. Having studied these relationships, E.M. Kvyatkov-sky concluded that the reserves of metals in deposits of three decimal ranked classes are roughly approximated by the empirical relationship $Q_{sm} = 10^6 C_C$, $Q_{med} = 10^7 C_C$ and $Q_{lar} = 10^8 C_C$. According to the refined data presented in Table 7, closer correlations (excepting Co) would mean an increase of these values by an order of magnitude. Much care should be exercised when interpreting these relationships in view of changing requirements by industry.

Sec. 1.7. The Relationship Between Geochemical Anomalies in the Different Geospheres

A deeply-seated occurrence of a producing deposit or of a deposit of little economic importance of any useful material, representing, as it does, a geochemical anomaly, may under definite conditions form lithochemical, hydrochemical, biogeochemical and atmochemical dispersion aureoles and dispersion flows. The supergene migration of elements in any of the geospheres may give rise to the formation of various secondary concentrations of chemical elements. Due to the continuous exchange between the geospheres, these geochemical anomalies are all closely interconnected.

It has been unambiguously established that there are hydrochemical anomalies in the composition of stream or subsurface waters in the vicinity of ore deposits, whatever their genetic type. Equally unquestionable is the likelihood of anomalous trace-element contents in vegetation growing in the mineralization zone, since it is the environment that is responsible for the composition of living matter. Studies undertaken by many workers in this country and elsewhere have proved the presence of anomalous concentrations of gases extruded from or trapped in surficial and deeply buried deposits of ores.

The interrelation and interdependence of geochemical anomalies occurring in the lithosphere, atmosphere, hydrosphere and biosphere and the character of the direct and reverse effects involved are illustrated diagrammatically by Fig. 11. The occurrence of an orebody and its primary halo in the lithosphere may be directly responsible for the formation of secondary dispersion aureoles in the products of weathering and overburden overlying these and of dispersion flows in the alluvial stream sediments. These geochemical anomalies represent, respectively, a primary and a secondary dis-

person related to targets of search, i.e. a deposit in the lithosphere.
Effusion and diffusion of gases emanating through mineralized zones
from the deeper reaches lead to the origination of gaseous aureoles
and dispersion flows in the underground and surficial atmospheres.
If we take into account lithochemical dispersion aureoles involved
in this process, we must regard gaseous anomalies as being a second-
ary and ternary dispersion associated with the target of search.
Gaseous constituents of the atmochemical aureoles participating
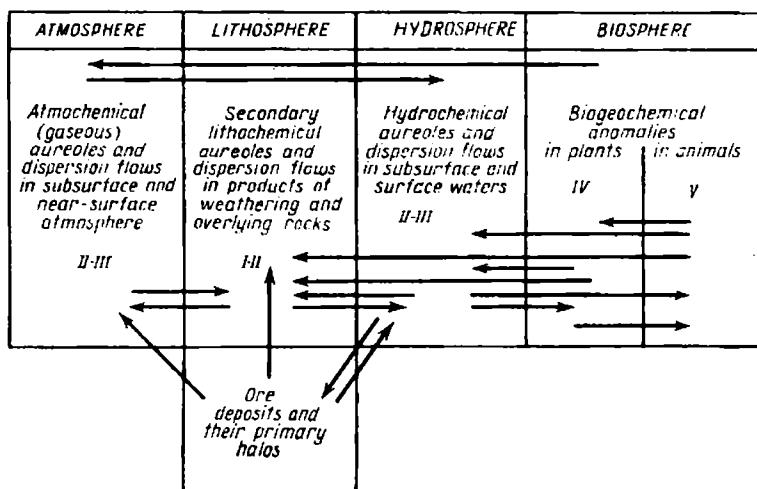in the chemical reactions in the oxidation zone undergo sorption

FIG. 11. Interrelation and interdependence of geochemical anomalies in the
geospheres:
I-V — degree of remoteness from target of search. Arrows show directions of feed and
backfeed

and occlusion to pass then to a solid phase which fact mirrors their
intimate connection with the lithochemical dispersion aureole.

Similar guides to a target of search are provided by geochemical
anomalies in the hydrosphere that form during mineral dissolution
as the result of the interaction between the subsurface waters and
primary ore deposit; of atmospheric precipitation and secondary
lithochemical aureoles; and of the stream waters with lithochemical
dispersion flows. These hydrochemical aureoles and dispersion
flows, wherever they penetrate, produce a reverse and active effect
on the primary orebody (e.g. forming secondary sulphide enrich-
ment zones) and on the lithochemical aureoles and dispersion flows.
They do so through chemical exchange reactions, co-precipitation,
sorption or evaporation. The interactions of the natural waters with
host rocks cause, in the general case, element equilibria distribution

to be shifted toward the solid phase. Vegetation growing in a mineralization area unable directly to associate solid mineral materials accumulates higher than average contents of ore elements from the aqueous aureoles and dispersion flows giving rise to local biogeochemical anomalies. This assimilation of ore elements by plants is not irreversible. It has been established that respiration by plants causes emanation into the atmosphere of volatile metalloorganic compounds which forms a biogenic component of atmochemical anomalies over ore deposits. Atmospheric precipitation causes these gaseous components to come back to the litho- and hydrosphere.

Annual natural litter fall followed by mineralization causes ore elements to return to the hydrosphere as soluble compounds or to the lithosphere as solid mineral remnants. The chain of these successive transformations continues toward animal species.

As we pass from lithochemical to hydrochemical and then to biogeochemical surveys (see Fig. 11) the associated relations between an ore deposit (target of geochemical exploration) and anomalies being located get more involved and remote, and the data of the surveys harder to interpret. Even "florometric" surveys fail to enable one to differentiate unambiguously between the biogeochemical aureoles and dispersion flows, and the discovered anomalous ore element contents in living organisms cannot be relied upon to pinpoint ore deposits by drilling bore holes and excavating test pits. Unlike biogeochemical and hydrochemical anomalies, the secondary lithochemical aureoles and dispersion flows and primary halos of deposits demonstrate distinct direct connections with ore bodies. Once discovered, a lithochemical anomaly permits appraisal of the potential of the prospective mineralization area and, by allowing concurrently for other factors, enables the prospector to locate sites for test pits and bore holes.

To work out a "zoometric method of prospecting", 3 200 animal species—mammals, birds and amphibians—have been analysed in mineralization areas of the Urals. The author of the study, accounting for the "zoometric" links with mineralizations he had disclosed, stated with full reason that amphibians feed on insects, these latter on plants, and plants grow on soils being enriched by metals emanating from deeply buried ore deposits. Yet, to enter the biosphere, ore minerals should first be dissolved. Thus, a "zoometric" anomaly is *the fifth* remote aureole (see Fig. 11) of an ore deposit. Clearly, biogeochemical prospecting by studies of animals holds no promise.

An ore deposit may concurrently exhibit litho-, hydro-, atmo- and biogeochemical anomalies. It is best, however, to use one, very seldom two, methods of geochemical exploration. Experience shows that lithochemical techniques are advantageous for most geological conditions of mineral occurrences. This will continue as long as industry will rely on extraction of useful materials from the litho-

sphere. As deeper seated reaches will be exploited and new advances
in analytical techniques will be made, we should expect the role of
the atmochemical surveys to increase, for it is in the gaseous phase
that the migration of chemical elements is the most intensive. In
mountainous areas where lithochemical prospecting yields fairly
good results, there is generally no need in resorting to hydro-, atmo-
or biogeochemical methods. In other instances use should be made
of such a method (sometimes their combination) of geochemical pros-
pecting that would prove the most efficient in geological and eco-
nomic terms.

If we are to compare the efficacy of various geochemical methods,
we must take into account the effective dimensions of anomalies
within the boundary of $C_0\varepsilon^3$ and the contrast characteristic, Eq. (10),
for weak geochemical anomalies if we assume these as guides to eco-
nomic mineral deposits.

Sec. 1.8. Geochemical Landscapes

Geochemical exploration of blind and concealed deposits of what-
ever genesis may direct its effort to appreciable depths below the
ground surface, from the viewpoint of modern processes referred to
a zone of relative geochemical quiescence (see Fig. 10b, d). Geochem-
ical prospecting for mineral deposits is much more commonly con-
ducted in surficial layers where the lithosphere comes in touch with
the atmosphere and hydrosphere where modern processes of mechan-
ical, soluble and biogenic migration are at work. As a result it is
the mechanisms of supergene migration of the chemical elements
that largely determine the choice of procedures of geochemical ex-
ploration and appraisal of the discovered litho-, hydro-, atmo- and
biogeochemical anomalies. These processes are the subject of the
studying of geochemical landscapes put forward by B. B. Polynov
[23]. It is based on concepts of *elementary landscapes, segments of the
earth's surface exhibiting uniform conditions of the supergene migration
of the chemical elements*, with homogeneous environmental and geo-
logical features and a definite type of relief, vegetation and soil.
Accordingly, he differentiates autonomous (eluvial) landscapes of
flat watersheds with a deeply lying water table; transeluvial (eluvio-
deluvial) landscapes of mountainous slopes; and supraqueous (above-
water) elementary landscapes manifesting a water table level close
to the ground surface. Paragenetic association of elementary land-
scapes that are interconnected through the migration of chemical ele-
ments gives rise to a local geochemical landscape. Essential extra-
neous factors of the supergene migration of the chemical elements are
the type of relief, absolute level and fluctuations of temperature, evap-
oration and atmospheric precipitation, physical disintegration and
weathering of rocks, dissolution and sedimentation, hydrolysis, oxi-

dation and reduction, growth and decay of plant and animal species. These factors, taken in various proportions, are best illustrated by climatic and vegetation zones that vary with the latitude and absolute elevation of the particular terrain. Accordingly, the classification of geochemical landscapes relies on a *bioclimatic* basis.

A. 1. Perelman divides geochemical landscapes into 4 groups in conformity with the peculiarities of the biologic cycle of aerial migrants (C, O, H, N): (1) forest; (2) meadow and steppe; (3) tundra; (4) primitive desert. Each of these groups, depending on the type of plant communities, volume of annually produced biomass, its composition and rate of decay of vegetation, falls into several *types* of landscapes.

The division of geochemical landscapes into *classes* is governed by the composition of typomorphic elements and aqueous migration ions (Ca, Mg, Na, Cl, S, HCO_3 etc.). Landscape zoning of areas according to the character of the vegetation cover (groups, types and families) from the standpoint of geochemical exploration is fairly convenient. This feature is distinctly indicative of the conditions under which search is to be conducted, whether in forested or steppe regions, tundra or desert. The biogeoclimatic characteristic concurrently predetermines the structure of a landscape which includes the importance and thickness of the horizons: the vegetation cover, modern crustal layers of weathering, the overlying soil layers and water table. Figure 12 gives examples of individual types of elementary landscapes. Classification of landscapes according to the composition of the major mineral components of natural waters is of much importance for the choice of methods of geochemical exploration [23].

Natural waters of a landscape can be grouped into 4 classes according to the pH value: (1) strongly acidic with $pH < 3$; (2) acidic and weakly acidic with pH from 3.5 to 6.5; (3) neutral and weakly alkaline with pH from 6.5 to 8.5; (4) strongly alkaline with $pH > 8.5$. Under natural conditions of a supergene zone weak acids (CO_2, organic acids) and strong bases (Na, K, Ca, Mg) are prevalent. That is the reason why landscapes exhibiting weak acidity (forest and tundra plain), neutrality (mountainous forest and mountainous tundra), neutrality and alkalinity (steppe and desert) are particularly extremely distributed. Aqueous solutions with marked acidity can be found only in individual localities, e.g. in an oxidation zone of sulphide deposits (H_2SO_4) or in areas of volcanic activity (HCl), strongly alkaline soils generally manifest sodium salinization (Na_2CO_3; $NaHCO_3$).

Redox conditions at the ground surface are due to the dominance of oxygen environment owing to free oxygen in the atmosphere, its dissolution in the waters of the particular landscape and liberated during photosynthesis of plants. The boundary of an "oxygen level" below which the medium does not contain any longer free oxygen

agrees with the groundwater table. Reduction conditions obtain when there is an abundance of decaying organic remnants, mainly vegetation, and products of the activity of microorganisms. There are reduction conditions without hydrogen sulphide present described as gleyish characteristic for marshes and reduction conditions with H_2S with a local distribution. An indication of the change in redox conditions is the coloration of rocks: red and brownish shades due to the presence of compounds of Fe^{3+} are characteristic of oxidation
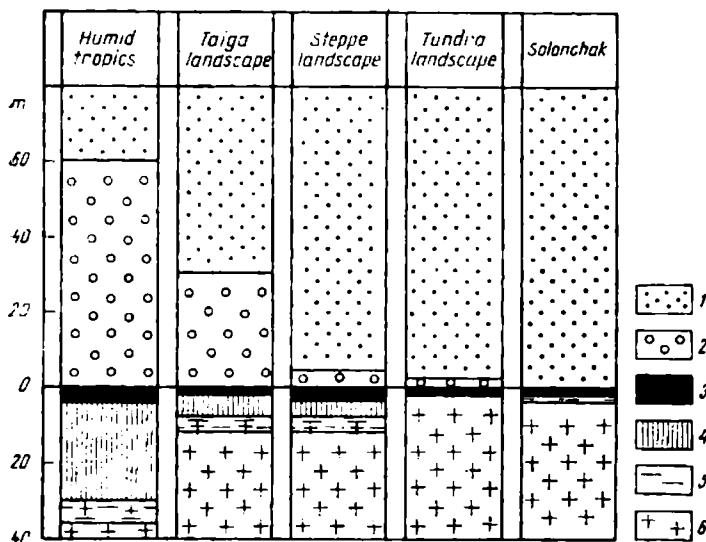

FIG. 12. Structure of elementary landscapes:
1 — near-surface atmosphere; *2* — vegetation cover and animal kingdom; *3* — soil; *4* — weathering crust; *5* — water table; *6* — bedrock

conditions, greyish green and dove-coloured shades characteristic of Fe^{2+} compounds correspond to reduction conditions. With alkalinity and at high temperatures oxidation reactions occur easier than in an acidic medium and at lower temperatures. This is, specifically, what is responsible for the prevalence of oxidation conditions in deserts and reduction conditions in tundra landscapes. In taiga acidic waters the boundary between the oxidation and reduction conditions is indicated by the Eh = +0.40, in alkaline steppe waters the limiting value drops to Eh = +0.15.

Absolute contents of chemical elements in waters cannot provide criteria of a capacity of elements to be dissolved since their contents in the lithosphere are different. This capacity is characterized by a coefficient of aqueous migration of elements proposed by A. I. Pe-

relman:

$$K_x = \frac{m_x 100}{a C_x} \qquad (28)$$

where m_x is the element content in water, g/l; a is the net mineral-ization of water, g/l; C_x is the element content in rocks containing the water, %.

A comparative characteristic of the rate of the migration of chemical elements is also provided by their thalassophily (affinity to sea) coefficients, i.e. the ratio of the clarke value of the given element in the hydrosphere to its clarke value in the lithosphere. The thalassophily coefficient τ_x, being an important value, is governed not only by the relative intensity of transition of an element to a solution, but also by the ensuing physicochemical and biogenic processes of its removal from oceanic water whose composition determines clarke values of the hydrosphere. Coefficients of the aqueous migration of the chemical elements are determined experimentally and provide characteristics of their behaviour in a particular geochemical landscape. From this viewpoint the values of K_x best characterize the importance of the aqueous migration of ore elements as supergene geochemical anomalies are formed.

The most intensive aqueous migration involves a group of active aqueous migrants ($K_x = n \times 10 \div n \times 100$) and a group of inert elements ($K_x \leqslant 0.0n$) whose behaviour practically is independent of the acidic alkaline or redox conditions of the medium. A separate group comprizes elements manifesting a contrast migrational capacity in the aqueous medium for which the values of $K_x \gtrsim 1$ are governed by the geochemical characteristic of the medium, primarily, by the pH and Eh. This element group with a variable valency is represented, e.g. by U and Mo liable to vigorous aqueous migration in an oxidation medium in a hexavalent form and which prove inert in a tetravalent form in reduction conditions. By contrast, under "gley" reductional conditions (without hydrogen sulphide) Fe^{2+} and Mn^{2+} in a divalent form are actively migrating in a solution. Under conditions of oxidation the same elements in a form of Fe^{3+} and Mn^{4+} are practically incapable of aqueous migration. The values of aqueous migration and thalassophily coefficients for the most important ore and some other chemical elements are presented in Table 8.

As can be seen from Table 8, aqueous migration is a principal form of transport of elements in the supergene zone with the values of $K_x > 10$ and $\tau_x > 1$ characteristic for Cl, S and Br. For boron, a typical aqueous migrant, the thalassophily coefficient drops to 0.4; and for iodine, owing to its biophilic nature, even to $\tau_x = 0.125$. F and Sr, relatively active aqueous migrants, possess even smaller values of the coefficient of thalassophily. All ore elements without

TABLE 8

Coefficients of Aqueous Migration K_x and Thalassophily τ_x of Definite

Active agueous migrants		Sluggish and inert migrants
$K_x = n \times 10\text{-}n \times 100$	$K_x = n$	$K_x = 0.1 - 0.01$ and less
Cl (111), S(1.9) Br (30), B (0.4), I (0.125)	F (0.0015) Sr (0.023)	Ba (3×10^{-5}), Rb, Li, P (5×10^{-5}), Sn (1.2×10^{-3}), Sb, As (8×10^{-3}), Al, Ti, Zr, Cr, Tr, Nb, Ta, W, Bi, Au (9×10^{-4}), Pt, Th (3×10^{-5})

Note. Parenthesized are values of τ_x.

exception manifest very small values of the latter coefficient, and their clarke values in the lithosphere are greater by a factor of several thousand and several hundred thousand than in the hydrosphere. The distinctly subordinate role of the aqueous migration of ore elements becomes apparent if we take into account the fact that many ore elements invariably exhibit low values of coefficients of aqueous migration, that natural waters of mountainous regions predeterminantly manifest a neutral or weak alkaline reaction (Zn, Cu, Ni, Pb... are inert), that decaying vegetable remnants produce reduction conditions (Mo, U... are inert) and that at the near-surface horizon oxygen conditions are prevailing (Fe, Mn, Co are inert). This does not imply that ore or rock forming elements characterized by the values of $K_x \ll 1.0$ are incapable of migrating in the supergene zone. On a scale very much exceeding that of aqueous migration these elements, as diverse natural mineral and nonmineral formations migrate in a solid phase under the action of mechanical aqueous and aeolian denudation of the dry land. These processes may be added to, to one degree or another, by the biogenic and gaseous migration of chemical elements. All these factors, whatever the values of coefficients of aqueous migration, add to elements a universal mobility in any geochemical landscape. The domination of mechanical migration of elements in landscapes of ore regions is substantiated by the average ratio between the moduli of solid and soluble load equal to 10 : 1 (see Sec. 2.1) which levels down the effect of different

Elements [22, 23]

Elements with a contrast migrational capacity $K_x \gtrless 1$	
Mobile and sluggish in oxidation conditions and inert in reduction conditions	Mobile and sluggish in reduction conditions (in absence of hydrogen sulphide) and inert in oxidation conditions

Migrating only in acidic waters:
    Zn (6×10^{-4}), Cu (4×10^{-4})
    Ni (5×10^{-5}), Pb (3×10^{-4}),
    Cd, Hg (3×10^{-4}), Ag
Migrating in acidic and alkaline waters:
    V (5×10^{-4}), U (8×10^{-4})
    Mo (9×10^{-4}), Se (8×10^{-2})
	Fe (1×10^{-6})
	Mn (4×10^{-6})
	Co (5×10^{-5})

coefficients of aqueous migration of the chemical elements. Under conditions of smooth relief features the role of mechanogenesis is decreased and the influence of peculiarities of the aqueous migration of elements and the aridity or humidity of the particular region on the formation of the landscape is enhanced. Generally small values of K_x and τ_x for ore elements and the predominant supergene migration of these in a solid phase provide additional proof of that the lithochemical method of exploration of ore deposits is of particular importance.

Elements, when dissolved, after a change in geochemical conditions, may be precipitated forming secondary concentrations. An area where there occurs an abrupt decrease in the intensity of element migration followed by element concentration is said to be a geochemical barrier [22]. Elements with a contrast migrational capacity are sedimented at physicochemical barriers. Active aqueous migrants precipitate following evaporation of the solution and elements with constant small coefficients of aqueous migration are liable to secondary accumulation according to density-dependent gravity classification of minerals during transport in a solid phase and mechanical sedimentation. Accordingly, we distinguish between the following main types of supergene geochemical barriers:

(1) evaporational (B, Sr, F, sometimes Mo);
(2) gravitational (Au, Pt, Sn, W, Nb, Ta, Ti, etc.);
(3) reductional (Mo, U, Se);

(4) oxygen (Fe, Mn);

(5) alkaline (Cu);

(6) adsorptional (Cu, Zn, Pb, U, Mo etc.).

The list of possible geochemical barriers is far from thus being exhausted. We have pointed out only the most important of these and presented such chemical elements whose supergene concentrations are discovered by geochemical prospecting. Whatever the geochemical barrier, the possibility of associated litho-, hydro- and biogeochemical anomalies is not ruled out. The accumulation of an ore element on a supergene geochemical barrier may sometimes take on such a scale as to enable the formation of an economic exogenic deposit of the particular element in the lithosphere as primary sedimented orebodies and placers, or in the hydrosphere as concentrated brines (Br, I). The sedimentation of elements on geochemical barriers applies as well to the endogenic migration, characterizing, e.g. a hydrothermal ore emplacement. Secondary ore-element accumulations at supergene geochemical barriers may appear as ore-free anomalies to be ignored in geochemical exploration. The characteristic permitting secondary aureoles and dispersion flows related to ore deposits to be discriminated from worthless material accumulations is provided by the appearance in the ore anomalies of high contents of elements whose co-precipitation is not typical of supergene geochemical barriers (Sr and Pb; Sn and Mo; Au and As etc.).

Particular attention should be drawn to landscape analysis during terrestrial lithochemical surveys in regions with concealed orebodies when probable ore anomalies over buried ore deposits are of commeasurable amplitude and are hard to distinguish from ore-free evaporational, sorptional and biogenic accumulations of trace elements.

Small-scale geochemical landscape zoning is essential for decision-making as to the particular techniques of geochemical exploration of ore deposits (see Chap. 6). One of its objectives, specifically, is to locate areas where it is not plausible to conduct terrestrial geochemical surveys in which case these must be supplemented or substituted by hydro-, atmo- or biogeochemical surveys, or lithochemical exploration should be directed to greater depth. Secondary lithochemical aureoles and dispersion flows from ore deposits are distinctly mirrored by the modern ground surface in mountainous areas, in various landscapes from arid steppes of the Middle Asia to the tundra of Chukotka. The complex of geochemical landscape conditions is quantitatively shown by the local values of the productivity coefficient $k \gtrless 1$ entering into Eqs. (18)-(19) and similar relations and characterizing the behaviour of the elements of interest to us. Local values of these coefficients materially contribute to the understanding of landscapes.

Sec. 1.9. Methods of Prospecting and Their Efficacy

The main requirement to be met by geochemical prospecting is that it must be consistent with the accepted procedures of geological investigation, from regional national surveys to detailed exploration of ore deposits. Accordingly, geochemical orientation surveys are first conducted on a small scale encompassing vast areas, then, basing on the data obtained, selected areas are surveyed. In so doing, the scales increase, and areas surveyed decrease. A transition from a small-scale survey to a detailed survey does not mean merely a repetition of search with closer spacing between observation points. Rather, both the procedures and objectives in mind are different.

1. Small-scale surveys are aimed at discovery of universal features characteristic of most deposits, e.g. large dimensions of geochemical anomalies providing guides to large mineral deposits. Detailed surveys take into account individual, often unique, features of each particular deposit.

|2. In a small-scale survey samples are collected from the media that are more *distant* from the target of search, say, lacustrine or stream sediments, natural waters or vegetation. With increasing the scale of the survey, the genetic nature of sediments being tested approaches that of the target of search. The last to be tested are the bedrocks and ores. The geologic survey of an area is conducted successively on scales 1 : 1 000 000, 1 : 200 000 and 1 : 50 000. The intermediate scales 1 : 500 000, 1 : 100 000 and 1 : 25 000 are seldom used. 1 : 10 000 and larger scales classed as special-purpose ones, are to be conducted only for reconnaissance of deposits or for engineering purposes. The same principal scales are used for reconnaissance and detailed geochemical surveys anticipating or jointly with geological mapping. Of the 22.4 million km^2 taken by the area of the USSR, some 7.0 million km^2 is occupied by mountainous regions where it is plausible to conduct various terrestrial and aerial geochemical surveys to locate outcropping ore deposits (see Fig. 10a). Another 3 million km^2 covered by sediments of recent origin up to 500 m in thickness permits terrestrial and subsurface surveys to pinpoint concealed ore deposits (see Fig. 10b). Geological exploration of the remaining area covered by a thick mass of platform sediments primarily involves prospecting for oil, natural gas and coal deposits, construction materials, hydrochemical sediments and placer deposits.

Geological mapping of the territory of the USSR on a 1 : 1 000 000 scale has been completed, and no orientation geochemical surveys are being conducted on this scale in the Soviet Union. Each of the stages of geological exploration and respective detailed reconnaissance surveys must conform to the purpose in mind. This latter may vary depending on how well the particular region has been investi-

gated from the economical and geological viewpoint. The objectives
of exploration of new regions are to locate only large or very large
deposits whose availability (other than of blind bodies) can be
readily proved.

The question arises as to how many large deposits can be expected
in the particular region. Since ore reserves vary from region to re-
gion, this question can be answered only if we refer to some averaged
data and rough estimates owing to our inadequate knowledge of the
actual reserves even of areas that have been sufficiently explored.
One may assume that one large deposit will occur, on the average,
per 10 thousand km² of a relatively well explored ore region.
Basing on this assumption and on the ratio between the numbers
of various ranked deposits (see Table 5), one may estimate the num-
ber of orebodies likely to be discovered in unexplored promising ore
regions if their dimensions are large enough to conform to the law
of large numbers. These will be deposits of such materials and of such
genetic types as to be expected to occur in a particular locality in
the context of its geological features, geological history and metallo-
genic properties. These and similar data are mirrored in geological
maps on a scale 1 : 1 000 000 or the adjacent smaller scale. The ef-
ficacy of prospecting operations is made possible by regular geochem-
ical surveys on a 1 : 200 000 scale encompassing large areas ($n \times 10^4$
to $n \times 10^5$ km²) without deliberately omitting any segments of the
ground surface. The latter follows from the geologist's rule: "There
are no barren areas, but, rather, areas that have and have not been
explored."

The next stage includes geochemical surveys on a 1 : 50 000 and
adjacent scales (1 : 100 000 to 1 : 25 000). These may be aerial,
terrestrial or deep-seated litho-, hydro-, atmo- or biogeochemical
surveys conducted to meet the requirements outlined in Sec. 1.7.
The objective of such surveys is generally finding secondary disper-
sion aureoles from deposits. Should they be carried out following
geochemical surveys on a 1 : 200 000 scale, they are needed for eval-
uation purposes. In mining regions, 1 : 50 000 scale geochemical
surveys of secondary dispersion aureoles may be conducted omitting
1 : 200 000 scale surveys. In the latter case the ultimate objective
of these operations, apart from pinpointing new large deposits, may
include search for medium and small deposits. The priority of a geo-
chemical survey on a 1 : 50 000 scale is governed by a variety of eco-
nomical and geological factors.

Having taken into account the data obtained, we proceed to pros-
pecting survey operations on a 1 : 10 000 scale, generally by the use
of lithochemical methods. By referring to maps of secondary litho-
chemical dispersion aureoles and primary halos related to ore ele-
ments, one can best site prospect trenches and boreholes to pinpoint
and sample the primary ore deposit.

If a prospect pit or borehole has revealed a minable occurrence, the geological task is considered as being positively solved. Further geochemical methods are decided upon in the course of prospecting operations and governed by the geological conditions of the discovered deposit. If a prospect pit only reveals a mineralization of no economic significance, detailed lithochemical sampling of wall rocks as exposed in test pits and boreholes may use as large as 1 : 1 000 to 1 : 200 scales. The data obtained are interpreted basing on the theory of the formation of primary halos of ore deposits and zonal ore deposition (see Chap. 4). Preliminary, detailed and prospecting surveys of blind orebodies at the flanks and deep horizons of minable ore deposits use the same scales and principles. This technique of starting geochemical exploration surveys on a regional small-scale basis and proceeding to detailed surveys is the most rational and universally accepted, which, however, does not rule out possible departures.

The estimates of the content of the material of interest to us that can be expected at an area (ore region or district) and of ore occurrences discovered should be expressed in terms of the probable reserves of the metal. This should be done at the beginning stages of exploration to substantiate transition to the following stages.

Whatever the degree of reliability, the method of calculating reserves may be assumed as adequate if the corresponding estimates of Q_H are unbiased estimates, diverging with an equal probability toward greater or smaller values from the true amounts of reserves

$$Q_H = Q_{tr} e^{\pm t} \qquad (29)$$

where $\varepsilon > 1$ is a standard factor governed by the detail of the survey; $t = 1, 2, 3 \ldots$ is governed by the confidence interval of the estimates. It should be borne in mind that the term "true reserves" Q_{tr} is merely conventional, the value being dependent on the chosen limiting content of the metal and depth of calculation which may differ from that of the predicted value H. Predicted (geological) amounts of metal in unexplored deposits to be expected in the area being studied are known as resources and, depending on the particular stage of survey operations, denoted as P_3, P_2 and P_1, as the confidence increases. Table 9 shows relationships between these predicted resources' categories, stages of geological exploration and scales of geochemical surveys. The data on minable reserves furnished by prospecting for a deposit pinpointed by referring to the geochemical evidence provide the only criterion of the efficacy of ore hunting, and the degree of convergence of these and predicted estimates provides a check on whether the geochemical data have been properly interpreted.

What is a unique feature of direct geochemical data is that they are objective and free from the effect of personal outlook of the pros-

TABLE 9

Stages of Geological Exploration and Estimates of Probable Resources
of Solid Minerals

Stage	Type and scale of geochemical survey	Category of resources
1. Regional geological exploration of the territory of USSR: (a) regional geological and geophysical investigations on scales 1 : 1 000 000-1 : 500 000; (b) regional geophysical, geologic survey, hydrogeological and geoengineering operations on scale 1 : 200 000 (1 : 100 000)	Regional geochemical mapping: terrestrial (1 : 200 000 and smaller), aerogeochemical (1 : 100 000 and smaller)	P_3
2. Geological surveys on scale 1 : 50 000 (1 : 25 000)	Aerial and terrestrial geochemical prospecting surveys (1 : 50 000-1 : 25 000 scales)	P_2
3. Prospecting operations	Geochemical deep-seated (1 : : 100 000-1 : 50 000 scales)	
4. Prospecting assessment operations	Detailed lithochemical mapping referred to secondary dispersion aureoles: terrestrial (1 : 10 000 and larger), deep-seated (1 : 25 000 and larger). Prospecting referred to primary halos (1 : 10 000 and larger scales)	P_1
5. Preliminary prospecting 6. Detailed prospecting 7. Additional prospecting of: (a) an intact ore deposit (b) workable ore deposit 8. Prospecting for exploitation	Geochemical investigations on scales 1 : 1000-1 : 200 by means of continuous testing of host rocks and ores referred to samples collected from prospect pits and cores	P_1-C_2

pectors. As a result, apart from locating new deposits, geochemical
surveys make it possible to prepare long-term maps permitting any
geological interpretation of the evidence available.

Lithochemical Dispersion Flows

Sec. 2.1. Solid and Soluble Load

Throughout the geological history of the earth, the dry land has been subjected to the concerted action of weathering and erosion. The latter processes, forming a supergene field of dispersion of mineral deposits, are what determines the development of secondary lithochemical aureoles and dispersion flows from mineral deposits that are essential for mineral exploration. The scope of the processes of erosion involving removal and transport of weathering products to the sedimentation zone can be inferred from the impressive bulk of evidence furnished by geology, physical geography and hydrology.

Of the 510 million km² of the surface of the globe 29% or 149 million km² is occupied by modern land. Only 0.8 million km² of the earth's surface is found below the sea level. The average elevation of land is 875 m, the ground surface presenting an assortment of lowlands, uplands and high mountain ranges. Terrestrial relief is constantly changing. There are numerous agents of various nature that shape the relief features. On the one hand, these are internal forces that cause displacements of huge blocks (cratons) of the earth's crust. Upheavals of individual crustal segments and large-scale tectonic disturbances have caused mountain building, i.e. positive (elevated) land forms. On the other hand, agents responsible for relief alternations are extraneous forces responsible for rugged topography and erosion of elevated portions of the earth's surface, transfer of the products of weathering and sedimentation in depressions. This reverse process of universal degradation of the earth's surface often leading to the formation of complicated relief features is caused by gravity. Its driving force is the energy of solar radiation.

At the boundary of the atmosphere the earth's surface receives an annual 7×10^{24} J of heat as solar radiation or an average 2.1 J per 1 cm² each minute. 42% of this amount is reflected back into space and 58% is absorbed by the earth's surface and atmosphere*. These huge quantities of radiant energy do enormous work at the earth's surface; they are responsible for the thermal regime of the sea and

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* Owing to back thermal (long-wave) radiation reflected by the earth, its thermal balance generally remains unchanged since the amounts of solar radiation received and returned back to space are mutually compensated.

atmosphere, shape the climatic conditions and provide a source of
life on earth. About half of the solar energy coming to earth is being
used for the evaporation of water. The subsequent condensation of
the water vapours in the atmosphere results in precipitation falling
on the earth's surface and responsible for the water balance of the
planet.

More atmospheric precipitation falls annually on the dry land than
is evaporated. This excess 36 thousand km^3 forms runoff. This runoff
causes land erosion owing to the dissolving power of aqueous fluids
and transport by them of erosion products to lower land forms.

Streams throughout the world are moving huge amounts of solid
material travelling in solution or suspension and sediments carried
over the stream bed collectively known as solid load. The amount
of the solid load washed annually to the world ocean is estimated
to be about 20 billion t. That of salts transported to the ocean from
land is roughly 2.7 billion t. The identical processes taking place in
intracontinental basins occupying 41.8 million km^2 or 27% of
modern land can be averaged by the same figures.

Land erosion by the stream action alone causes lowering of land,
on the average, by 1 m every 10 000 years, or, to put it differently,
every year land loses 260 t of solid materials per 1 km^2 of its area.
This value, termed *an annual layer of denudation* is presented for
various territories (in mm/yr) as follows:

Asia 0.14
Europe 0.05
Russian plain 0.03
US plains 0.04
Greater Caucasus 0.7
Alps 0.86
Volga basin 0.005
Danube basin 0.1
Rhône and Po basins 0.27
Amu-Darya basin 0.96
Vakhsh basin 1.63
Island Java . . . .   up to 2.0
Island Kalimantan (Borneo) 4.0

The extreme values varying by a factor of 1 000, the annual layer
of denudation may be much less, agree with or appreciably exceed
the average rate of the lowering of the surface of land (0.1 mm/yr).
Moreover, individual low-lying areas of land may exhibit an increase
in level owing to the accumulation of sediments.

The stream activity is not the sole factor responsible for the degra-
dation of the earth's surface. The non-uniform heating of the atmo-
sphere by solar radiation in different latitudes and above land or sea
causes winds, i.e. continuous movement of air. The winds carry
huge amounts of suspended dust particles or roll larger rock frag-
ments. The activity of the wind may sometimes be opposite to the

transporting activity of streams invariably carrying the eroded materials only to low-lying regions, and, in the general case, to the world ocean.

Lithochemical dispersion flows from mineral deposits originate in the dry land due to the driving force and dissolving capacity of water as a result of gravity-induced transport of weathering products toward lower relief forms and sedimentation areas. Of lesser importance is the activity of modern glaciers, yet in the geological past northern regions of Europe, Canada and Alaska witnessed an essential role played by glaciers the traces of whose activity can still be seen at present. An appreciable role in the formation of dispersion flows in Alpine regions is played by screes, rockfalls and rock streams, in subpolar areas solifluxion may prove of specific importance. The transporting power of the wind, with very rare exceptions, is unable to produce any distinct lithochemical dispersion flows.

The dominant role of lithochemical dispersion of ore elements and the ancillary role played by hydrochemical processes are particularly distinct in the formation of dispersion flows from most ore deposits in most localities. The distribution of the chemical elements in the dissolved and the solid phase, are characterized by the respective coefficients of aqueous migration and thalassophily (cf. Table 8). Excepting oxygen and hydrogen, clarke values of oceanic water exceed those of the lithosphere only referring to three elements, Cl, S and Br. All the other elements are not accumulated in the hydrosphere and mostly occur in stream sediments. Referring to the deficit of many chemical elements in the hydrosphere, A. A. Saukov wrote: "Had there been in the earth's crust no mechanisms for control of supply of the chemical elements to the seas and oceans and had all the elements contained in the end products of weathering had no difficulty of penetrating into the hydrosphere, the composition of the latter would have been different from what it actually is. In particular, the abundance of zinc, lead, mercury, arsenic, copper and selenium would have been hundreds and thousands of times greater" [31]. This list of elements can be augmented by Sn, W, Ni, Mo, Cr, Au, Pt, Th and many other elements the deposits of which are general targets of geochemical exploration. The predominance of lithochemical dispersion in the alluvial dispersion flow as well as on the periphery of eluvio-deluvial aureole of an ore deposit is conditioned by these factors:

(1) the tendency for exchange chemical reactions in water solutions to form compounds that are the most difficult to dissolve and are weakly dissociating;

(2) the precipitation from the solution of most heavy metals already at the $pH < 5.5$ whereas the waters of mountainous streams and rivers generally show $pH \geqslant 7$;

(3) the sorption of cations of metals by mineral and organic colloidal suspensions of finely dispersed silt and clayey fractions of alluvium.

A classical method of studying mechanical dispersion flows is a heavy concentration survey. Its applications, however, are limited by prospecting for deposits of minerals exhibiting such a high density (>4 g/cm^3) and chemical and mechanical resistance as to be able to be concentrated by panning. This circumstance caused the prospectors, following the elaboration of methods for lithochemical exploration of dispersion aureoles of ore deposit, to work out techniques for locating dispersion flows of nonferrous and rare metals deposits whole minerals are other than exhibiting typically heavy concentrations (Cu, Ni, Co, Ag, Pb, As, Zn, Mo, U and others). It has been long established that it is expedient to explore the solid material in the solid runoff for these purposes. According to the data of Strakhov on the forms of transport of the main constituents of the stream load (Fig. 13), the migration of ore elements in molecular solutions is of a subordinate nature. The total ratio between the net solid
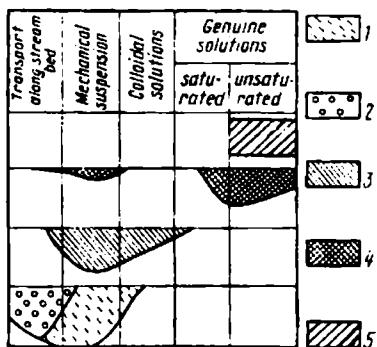
FIG. 13. Forms of transfer in rivers of principal sediment constituents:

1 — clay minerals; *2* — aleurolite and sand minerals; *3* — iron, manganese, phosphorus, most minor elements (V, Cr, Ni, Co, Cu ...); *4* — Ca, Mg carbonates; *5* — K, Na, Ca, Mg chlorides and sulphates

and suspended residue in streams, on the one hand, and the soluble load, on the other, is estimated by him for mountainous regions to be 7.66 to 1.0. The domination of the soluble load is observed only for lowland rivers (the Neva, the Volga, the lower reaches of the Lena River etc.) where no exploration of ore deposits from their dispersion flows is carried out. On the whole, mechanical and chemical erosion are particularly pronounced in humid areas with an average annual temperature above $+10$ °C and are intimately linked with the degree of ruggedness of topography and the tectonic activity in the particular locality. The mechanical transport of Fe, Mn, P and trace elements (V, Cr, Ni, Co, Cu etc.) in mountain rivers may often "prove to be the only form of transport of any significance". What has been said above does not rule out the probability of formation of anomalous concentrations of ore elements in river waters for there is an intimate relationship between the formation of geochemical anomalies in the different geospheres (cf. Sec. 1.7). What we want to emphasize is that the solid phase materials are predominant in the dispersion flows of ore deposits. An essential role of river transport of As and

Mo as a soluble load has been found in the Transbaikal Region; no doubt, it is also appreciable for B, F, Sr and Li; sulphur of sulphide deposits is migrated in river waters as a sulphate ion. Summing up the methods of geochemical prospecting for ore deposits by referring to their dispersion flows in the drainage water, one can assume that the walls of the container, i.e. the solid material of the rocks forming the banks or stream beds, beds of rivers and springs should be sampled for exploratory purposes. This conclusion does not rule out the existence of such geochemical conditions under which it is the most reasonable to resort to a hydrochemical prospecting for particular useful components (cf. Sec. 5.1).

Sec. 2.2. Ideal Dispersion Flow Equations

Let us calculate the metal content in a lithochemical dispersion flow for a randomly chosen deposit whose secondary residual dispersion aureole is subject to current processes of denudation on the slope of a valley. Let us define as a flow of order I any river (stream, river bed) without tributaries. According to this classification, two rivers
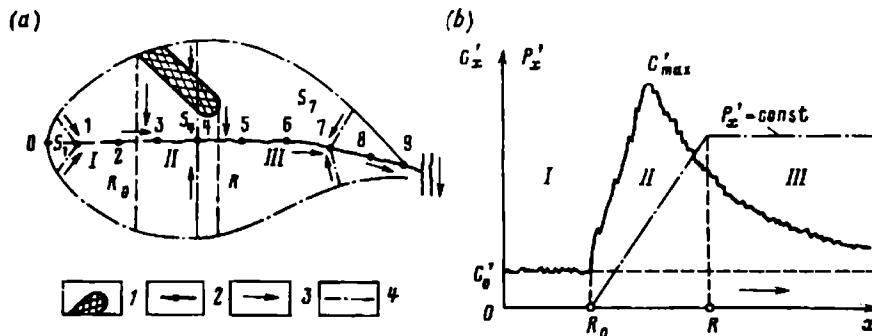
FIG. 14. Concerning the calculation of a dispersion flow:
a — position of the orebody in the catchment basin; *b* — dispersion train graphs; *1* — secondary residual dispersion aureoles with productivity *P*, m^2 %; *2* — sampling points of alluvial sediments; *3* — direction of runoff; *4* — boundaries of catchment basins S_x. Roman numerals denote intervals bounded by points of beginning (R_0) and end (R) of supply of metal to the stream bed from the dispersion aureole

of order I merge to form a river of order II; two order II rivers merge forming an order III river which, in turn, may take as tributary streams only order I and II rivers etc.

The catchment basins of order I river beds most typically are of a pear-shaped configuration and their area S_x for any point of the river bed increases in proportion to the squared distance x from the watershed apex 0 (Fig. 14). Suppose that on the slope of this valley there exists a secondary residual dispersion aureole with an areal

5*

productivity P m^2 % of metal. It is required to find the relationship between the metal content C'_x* in stream sediments and the coordinate of the sampling point:

$$C'_x = f(x) = f(P,\ S_x) \tag{30}$$

where P is a local parameter; $S_x = \varphi(x)$. In conformity with the above data it is permissible to consider the formation of a dispersion flow as totally represented by a solid load. In the stream bed shown in Fig. 14 we must distinguish three intervals: one, 1, located upstream from point R_0 where no ore material from the dispersion aureole comes from another, II, between points R_0 and R within which the metalliferous material coming from the left-hand slope onto the stream bed is responsible for the appearance of higher-than-average content of metal in the alluvium; and still another, III, downstream from point R, in which the alluvium is being added to only by the material eroded from both ore-free slopes due to which fact the anomalous metal content gradually diminishes.

Clearly, the metal content value remains identical with the background at all sampling points over interval I of the stream bed, and Eq. (30) assumes this form:

$$C'_x = C'_0 \tag{31}$$

In the first approximation alluvial sediments represent a natural average sample characterizing the entire spectrum of rocks and the presence of orebodies in the denudation basin of the particular stream.

Over interval III the metal content of the alluvium will exceed the background value by the amount

$$\Delta C'_x = \frac{q_{met}}{q_{rock}} \times 100\%$$

where q_{met} is an added amount of metal coming to the stream bed as a result of the decay of the dispersion aureole; q_{rock} is the total amount of material washed off within the same period of time from the entire catchment area S_x corresponding to the sampling point at a distance x from the apex of the watershed.

If we denote the average layer of denudation as Δh, we have

$$q_{met} = P\Delta h\ d \times 10^{-2}$$

$$q_{rock} = S_x \Delta h\ d$$

where d is the volume mass of the eroded material carried to the stream bed.

Hence $\Delta C_x = P/S_x$

$$C'_x = \frac{P}{S_x} + C'_0 \tag{32}$$

---

* Letter symbols for quantities relating to dispersion flows are generally primed (see Notations).

Over interval II the stream bed will be receiving different amounts of metal conditioned by the productivity P_x of the fraction of the dispersion aureole which is involved in the solid load at a sampling point x. To simplify matters, we assume the linear productivity of the aureole over the entire interval $R - R_0$ as remaining constant, thus $P_x/P = (x - R_0)/(R - R_0)$. Thence, by virtue of Eq. (32), we have

$$C'_x = \frac{P_x}{S_x} + C'_0 = \frac{P (x - R_0)}{S_x (R - R_0)} + C'_0 \tag{33}$$

Equations (31), (32) and (33) characterize the distribution of the metal content in an ideal lithochemical dispersion flow. Each of these relationships corresponds to a particular interval of a stream bed and they are incompatible in analytical terms.

A solution of Eq. (32) with respect to P yields

$$P = S_x (C'_x - C'_0) \tag{34}$$

Equation (34), characterizing an ideal dispersion flow, in real conditions is substituted by a proportional relationship. If we denote the right-hand side of Eq. (34) as P' and call it, analogous to the identical parameters of aureoles and orebodies, *the productivity of the dispersion flow*, we may well write:

$$P' = S_x (C'_x - C'_0) = k'P = \text{const} \tag{35}$$

where $k \gtrless 1.0$ is a proportionality coefficient governed by the local orohydrographic conditions and characteristic properties of the chemical elements in hand, particularly, the actual ratio between the solid and the soluble load.

Should the relative amount of the runoff of rock-forming minerals exceed that of the ore element compared with the ratio between them in the eluvio-deluvium, the alluvium becomes enriched by the ore element and its load increases accordingly. The metal content in the alluvium C'_x at which there appears a dynamic equilibrum between the inflow and discharge is what determines the value $k' > 1.0$. In case the total ore element runoff exceeds that of petrogenic elements owing to the small density of the former, liability to excess fragmentation or pronounced solvability, the local proportionality coefficient assumes the value $k' < 1.0$.

Since we did not restrict ourselves by any assumptions as to the shape of a catchment basin as we were deriving Eqs. (32)-(35), these may, in principle, be applied to stream beds of order II and higher orders. Accordingly, in any ideal lithochemical dispersion flow we may distinguish: an interval of ore element background values $x \leqslant$ $\leqslant R_0$ over which for all points the productivity of the dispersion flow P'_x is equal to zero; an interval of anomalous metal content val-

ues $R_0 < x \leqslant R$ due to the metal inflow from the slope onto the stream bed where the productivity of the flow is continuously increasing; an interval $x > R$ over which anomalous metal content values diminish, asymptotically approaching the background value, and the productivity of the dispersion flow remains constant. These relationships are illustrated by Fig. 14 and the data presented in Table 10.

TABLE 10

Characteristics of an Ideal Dispersion Flow

Interval of values x	Metal content in dispersion flow C'_x	Productivity of dispersion flow $P'_x = S_x (C'_x - C'_0)$
I $0 < x \leqslant R_0$	$C'_x = C'_0$ (background)	$P'_x = 0$
II $R_0 \leqslant x \leqslant R$	$C'_x = \dfrac{P(x - R_0)}{S_x (R - R_0)} + C'_0$ (anomalous-increasing and diminishing)	P'_x increases
III $x \geqslant R$	$C'_x = P/S_x + C'_0$ (anomalous — diminishes asymptotically approaching background)	$P'_x = k'P = \text{const}$

Graphs of $C'_x = f(x)$ referred to $C'_x \geqslant C'_A$ make it possible to locate only point R_0, the origin of inflow of an ore element from the dispersion aureole to the stream bed. It is not feasible to locate point R, determine the number of orebodies or estimate a relative scope of mineralization in the drainage basin by referring to metal content graphs even if order I stream beds are being sampled. These important additional data for areas with anomalous metal content values in the stream bed can be obtained by analysis of graphs of the productivity of dispersion flows $P'_x = f(x)$.

In conformity with Eq. (35), the productivity of the dispersion flow in interval III of the stream bed theoretically remains constant (see Fig. 14) showing a general tendency to diminish in actual dispersion flows. That is why the graph of the productivity of the dispersion flow allows the location of point R from the index of growth discontinuation P'_x, and from the value $P'_x = \text{const}$, allowing for the local value of k', permits the appraisal of the areal productivity of secondary dispersion aureoles developed within the particular drainage basin. The latter circumstance has direct bearing on the estimates of the area of the expected primary mineralization in confor-

mity with the relationship

$$P_p = \frac{1}{k'k} P'$$ (36)

Let us consider in more detail the expected shape of graphs of $C'_x = f(x)$ depending on the position of the secondary dispersion aureole in drainage basins of different forms. To solve this problem, it is convenient to align in plan the line of the stream bed with the abscissa axis taking it concurrently as being the symmetry axis of the valley, and for the watershed boundary contouring the drainage basin, to select an algebraic multinominal $y = \varphi(x)$ approximating the shape of the real catchment basin. In this case the catchment area S_x necessary for calculating the dispersion flow will be expressed for any point of the stream bed through an integral of a straightforward form

$$S_x = 2 \int_0^{x_i} \varphi(x) \cdot dx$$

For example, order I stream bed basins, like one represented in Fig. 14, are satisfactorily contoured by a curve of $y = x - \frac{1}{2b} x^2$ and, consequently, catchment areas for the corresponding sampling points can be calculated by referring to the following relationship

$$S_x = x^2 - \frac{1}{3b} x^3$$ (37)

where $2b$ is the length of the stream (note that b has the dimensionality of the length, so the right-hand side of the last relationship retains the dimensionality of the area).

The dispersion flow of an orebody located in such a drainage basin for $b = 1.0$, given the stream bed interval $R_0 \leqslant x \leqslant R$, by virtue of Eq. (33), will be determined from the relation

$$C'_x = \frac{3P(x - R_0)}{(3x^2 - x^3)(R - R_0)} + C'_0$$ (38)

For constant values of P, graphs of metal content C'_x in a dispersion flow, depending on the location of points R_0 and R will be of essentially different forms. The assumption made, Eq. (37), as to the shape of a basin, schematically modelling erosion-induced ruggedness of topography will not influence further conclusions. The shape of a drainage basin may as well be approximated by a triangle, square or ellipse, the areas of which increase in proportion to the square of one of linear dimensions. A very characteristic shape is exhibited by a population of curves calculated for different positions of the point where metal starts to be deposited in the stream

bed $R_0 = 0.0$; 0.1; 0.2 ... 0.9 at constant values of $R = 1.0$ and
$P = 100$ (Fig. 15). What is specific for them is that there is a pro-
nounced peak of the metal content in the upper reaches of a stream.
It is possible to locate points with the maximum metal content and
the value of this content C'_{max} in the dispersion flow by differentiating
Eq. (38) and equalizing the derivative to zero. It can be easily shown
in the long run that the actual maximum metal content in a disper-
sion flow is shown by graphs only for the value of $R_0 < 0.35R$. For
even given values that $R_0 =$
$= 0.35R$ the extreme point has
a coordinate $x > R$ and, conse-
quently, lies in the imaginary
region. A similar population of
curves with maximum values of
C'_x in the region of $x < 0.35$ is
manifested by graphs of metal
content $C'_x = f(x)$ for a constant
length of a dispersion flow
$R - R_0 = 1.0$ and joint succes-
sive translation of points R_0, R
from the apex of the watershed
toward the valley outlet. Graphs
of metal content C'_x do not show
any actual maximum in the lower
reaches of a stream. For all points
which are found a distance $x > R$
from the watershed apex and,
consequently, downstream from
the site of the actual influx of ore
material, the metal content in
the dispersion flow will be pro-
gressively decreasing in confor-
mity with Eq. (32). Viewed in

FIG. 15. Family of $C'_x = f(x)$ curves
for different positions of point $R_0 =$
$= 0.0$; 0.1; 0.2; ... 0.9 for $C'_0 = 0$;
$P = 100$; $R = 1.0$ and $S_x = x^2 - 1/3x^3$.
Arrow shows the direction of runoff

geometrical terms, this relationship presents a hyperbola with an
argument S_x. Figure 15 gives the corresponding segment for a case
where S_x satisfies Eq. (37). This hyperbola is *the common continua-
tion* for the entire population of curves, Eq. (38), with which they
have a common point $x = R$.

The limitations of analysis of ore element content and the impor-
tance of analysis of the productivity of dispersion flows can be in-
ferred from the following example. Figure 16 is a diagrammatic il-
lustration of two different locations of secondary dispersion aureoles
in a drainage basin. The areal productivity of the first dispersion au-
reole is assumed to be twice smaller than that of the second one. The
metal content C'_x and productivities P'_x of dispersion flows are calcu-
lated for each of the cases, given $k' = 1.0$. As can be inferred from

the presented graphs, if we had considered the metal content alone, we would have been erroneously attracted by the first case displaying a higher metal content value and longer extent of anomalous metal contents in the stream. It is by analysis of productivity of dispersion flow graphs that we would have been able to correctly estimate a greater promise offered by mineralization in the second case. It is worth noting that estimation of the results of heavy concentration surveys still relies on the principle: "weighable quantities (of an ore mineral
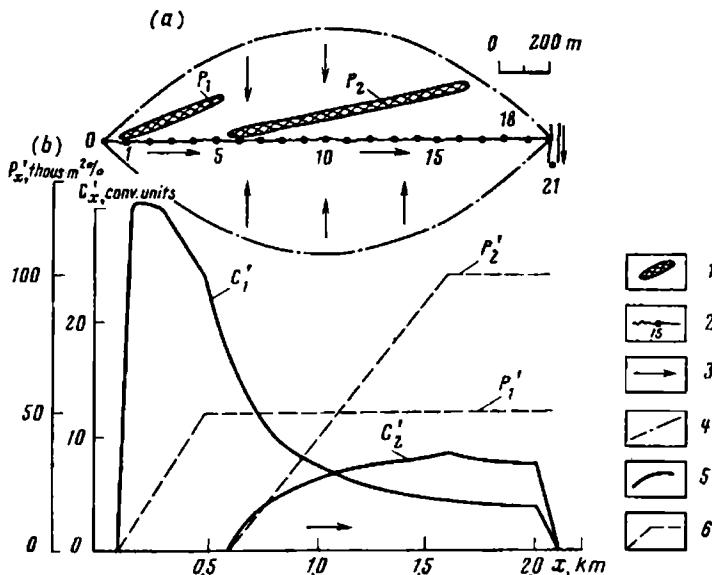
FIG. 16. Two versions of location of orebodies in the catchment basin (a) and dispersion flow graphs (b):

1 — secondary dispersion aureoles with productivity $P_2 = 2P_1$; *2* — sampling points; *3* — direction of runoff; *4* — boundary of basin. Graphs: *5* — metal contents (minus background); *6* — productivities of dispersion flow

in a heavy concentration sample) mean good results, trace quantities mean bad results". It appears clear that the criterion which has been used for centuries is insufficient.

Dispersion flows associated with a large mineralization zone can develop in a few adjacent streams. The total productivity of such a group of dispersion flows will be given by a sum of productivities of individual flows allowing for the successive merging of the stream bed with the values of $P_x' = $ const. The index characteristic $P_{tot}' = $

$$= \sum_{i=1}^{m} P_i'$$ applies not to an individual stream bed, but a particular geological object, an ore deposit giving rise to dispersion flows in m ad-

jacent stream beds. The estimate of a new target of search will be
provided by the values of prospective reserves of metal Q'_H calculated
to a reasonable depth. Such estimates are permissible only after a
geological examination *in situ* which makes it possible to determine
the genetic type and mode of occurrence of the discovered mineral-
ization (*cf*. Chap. 6). What underlies the estimated values of reserves
of metal from geochemical exploration data is a proportional rela-
tionship, Eq. (36), between the productivity of a primary mineral-
ization P_p and the productivity of lithochemical aureoles and flows
(P; $\Sigma P'_i$ $m^2\%$). For relatively steeply inclined (other than horizon-
tal) orebodies (see Fig. 9) this allows extension of the estimate of P_p
to an adequately chosen depth H according to this relationship:

$$Q'_H = \frac{1}{k'k} \times \frac{1}{40} H \sum_{i=1}^{m} P'_i \qquad (39)$$

where k' and $k \geqslant 1.0$ are local proportionality coefficients found ex-
perimentally. The division by 40 corresponds to transition from
quadratic metre percent to tonnes of metal.

Sec. 2.3. Formation of Real Dispersion Flows

Equations (32)-(33) and the ensuing relationship $P'_x = S'_x (C'_x - C'_0)$ = const at $x > R$ are of fundamental significance for a theory
of the formation of lithochemical dispersion flows related to ore de-
posits. They are based on an assumption that the allivium, at any
point of a stream bed, in terms of its chemical composition is a na-
tural average sample indicative of the composition of rock and ore
materials making up its denudation basin. In mountainous areas
this condition is not inconsistent to the general trend of processes
involved: the migration of petrogenic and ore elements generally
occurs in the form of a solid load. In mountain stream beds the erod-
ed materials washed from the slopes are being turbulently stirred
and the resultant alluvium is completely being moved out of the
boundaries of the mountainous region.

Mountain stream valleys invariably contain boulders, sandy pebble
and silty clay material from which silt samples are collected in litho-
chemical prospecting. Alluvial material sedimentation does not,
naturally, result in gradually filling up mountain stream valleys.
During lengthy geological periods erosion progress in a mountainous
area occurs under conditions of a dynamic equilibrium between the
introduction of eroded material from a slope to the river bed and its
removal, or if neotectonic events are under way, tends to conform to
a regular regime.

As lithochemical dispersion flows form, the stream bed represents
not only a region where there occurs stirring and transport of loose

material but provides concurrently a temporary base level of deposition. It must be noted that a larger role, compared with an idealized picture, is played in the formation of the local alluvium by material from the nearest slopes. As a result, over the interval where ore material is transported from the slopes to the stream bed the value of P'_x as computed from Eq. (34) is in excess of the true value of the productivity of the dispersion flow. In the lower reaches, rather than showing constant magnitudes, the value of P'_x rapidly diminishes. Thus it becomes impossible to record stable values of productivities of the dispersion flows and to estimate prospective reserves of metal by referring to Eq. (39). Under such conditions the values of P'_x as obtained from Eq. (34) should be termed *an apparent* productivity of the dispersion flow *the true* value of which, P'_{tr}, remains unknown. To provide a way out, A. N. Bogolyubov [20] and V. V. Polikarpochkin [20, 24] have proposed relevant solutions. Their methods, however, have not found practical use. What follows outlines a solution satisfying practical requirements.

The difference between the composition of stream sediments being sampled and that of a natural average sample of the entire denudation basin is conditioned by a variety of factors. It would be of no use to attempt separately to determine the effect of each of these on the formation of lithochemical dispersion flows. The only thing that is reasonable under such conditions is to characterize the complicated relationship by introducing a special coefficient that would substitute the sum of the active factors. Let us then introduce a dimensionless coefficient $\alpha' \geqslant 1.0$ characterizing the times the material of the adjacent slopes has been supplied to the alluvium compared with its expected part in the composition of a natural sample. We will further term α' a "slope coefficient of the alluvium".

Let us denote as C'_x and C'_{x-1} the ore element content in the adjacent sampling points the second of which is found upstream and, accordingly, has a catchment area $S_{x-1} < S_x$. The role of the local slope material in the alluvium of the particular stream bed is α' times greater than it would have been if we had referred to a natural average sample. That is why the ore element content at a point x will correspond to a weighted mean in proportion to the supply of metal to the segment of the stream bed $C'_{x-1} \cdot S_{x-1}$ and from the adjacent portion of the slope $S_x - S_{x-1} = \Delta S_x$. By assuming that at this portion of the slope there exist secondary dispersion aureoles whose productivity is ΔP_x and taking into account the background values, we have

$$C'_x = \frac{C'_{x-1} \times S_{x-1} + \alpha' \Delta P_x + \alpha' C'_0 \Delta S}{S_{x-1} + \alpha \Delta S} \qquad (40)$$

It can be readily seen that for values of $C'_{x-1} = C'_0$, $\alpha' = 1.0$ and $\Delta P_x = P$ this relationship reduces to the form of Eq. (32). It also follows from Eq. (40) that for $S_{x-1} = 0$ the magnitude of C'_x is no

longer governed by α' and, whatever its values, the straightforward relationship (35) is observed. This conclusion is in full agreement with the observational data according to which for minor catchments areas S_{R_0}, typical of order I-II stream beds graphs of productivities of real dispersion flows are fairly well approximated by one shown in Fig. 16. By assuming $C_0' = 0$ which is in principle equivalent to the value of C_x' minus background values, eliminating the denominator and introducing the notation $C_x' - C_{x-1}' = \Delta C_x'$, we obtain

$$S_{x-1} \Delta C_x' + \alpha' C_x' \Delta S - \alpha' \Delta P = 0$$

After dividing by ΔS and passing to the limit $\Delta S \to 0$ at which $S_{x-1} \to S_x$ we will obtain a differential equation of the process which is obeyed by the formation of the real dispersion flow

$$S_x \frac{dC_x'}{dS_x} + \alpha' \left(C_x' - \frac{dP_x}{dS_x} \right) = 0 \tag{41}$$

This relationship describes the connection between the productivity of secondary dispersion aureole on the slope and the ore element content in the alluvium throughout the length of the stream bed as long as the slope coefficient α' remains constant whether or not the slope exhibits anomalous mineral values. Over the entire interval of the stream bed from point R_0 to point R metal from the slope, in conformity to the adopted model, is being supplied uniformly, or $\frac{dP}{dS} = \frac{P}{S_R - S_{R_0}}$. A substitution of this relationship into Eq. (41) and division of the variables yields

$$\frac{dC_x'}{C_x' - \dfrac{P}{S_R - S_{R_0}}} = - \alpha' \frac{dS_x}{S_x}$$

By integrating this relationship and eliminating logs we have:

$$C_x' - \frac{P}{S_R - S_{R_0}} = A S_x^{-\alpha'} \tag{42}$$

where A is the result of taking antilogs of the integration constant.

Let us find the value of A for a point $S_x = S_{R_0}$ at which $C_x' = 0$. A substitution of A into Eq. (42) and its solution with respect to C_x', allowing for $C_0 = 0$ yields:

$$C_x' = \frac{P}{S_R - S_{R_0}} \left[1 - \left(\frac{S_{R_0}}{S_x} \right)^{\alpha'} \right] + C_0' \tag{43}$$

Throughout the extent of the stream bed downstream from point $x = R$, over interval III of a dispersion flow $\frac{dP}{dS} = 0$, whence $\frac{dC_x'}{C_x'} = = -\alpha' \frac{dS_x}{S_x}$.

By integrating this relationship we have

$$\ln C'_x = -\alpha' \ln S_x + B \qquad (44)$$

where B is an integration constant.

Let us determine its value as far as point $x = R$:

$$B = \ln C'_R + \alpha' \ln S_R$$

By substituting the value of B into Eq. (44), eliminating logs and solving it with respect to C'_x, allowing for $C'_0 \neq 0$, we have

$$C'_x = \frac{(C'_R - C'_0)}{(S_x/S_R)^{\alpha'}} + C'_0 \qquad (45)$$

The relationships (43) and (45) are equations of a real lithochemical dispersion flow, respectively, for its intervals II and III. Figure 17 presents graphs of the ore element content $C'_x = f(S_x)$ and of
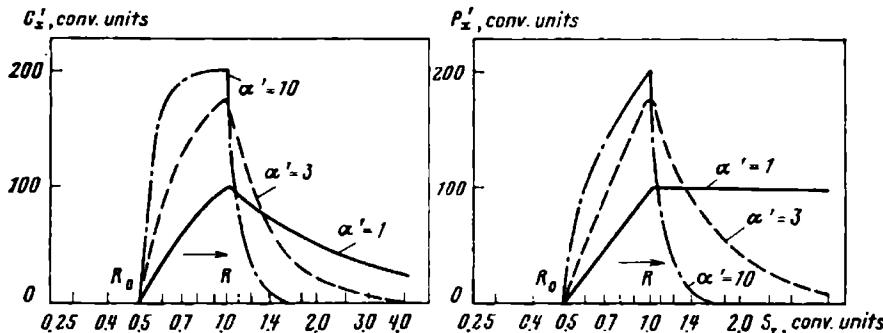
FIG. 17. Graphs of $C'_x = f(S_x)$ and $P'_x = f(S_x)$ of true (at $\alpha' = 1$) and apparent (at $\alpha' = 3$ and $\alpha' = 10$) productivity of dispersion flows
Arrows show the direction of runoff

productivities $P'_x = f(S_x)$ of dispersion flows for different values of $\alpha' \geqslant 1.0$ for $S_{R_0}/S_R = 0.5$ calculated by using these relationships. In the particular case maximum values of the apparent productivity twice as large as its true value.

A population of curves P'/P'_{tr} shown in Fig. 18 is indicative of the relationship of the apparent productivity and the position of point R_0. Since for $S_{R_0} = 0$ the productivity of a dispersion flow at point R equals the true value, although with $\alpha' > 1.0$ the condition $P'_x = \text{const}$ is not satisfied and below R a characteristic drop in productivity is to be observed. Given values $S_{R_0}/S_R = 0.8$, for the specified value of $\alpha' = 10.0$ the apparent productivity is almost five times as great as the true one, and as S_{R_0}/S_R is approaching 1.0 this increase is progressively growing. The interpretation of such

dispersion flows in quantitative terms calls for the determination of their true productivity so that it can be allowed for as a term in $\Sigma P'_i$ determining the total productivity of the discovered deposit.

By solving Eq. (45) with respect to α' we get

$$\alpha' = \frac{\log\left(\dfrac{C'_R - C'_0}{C'_x - C'_0}\right)}{\log(S_x/S_R)} \qquad (46)$$

The location of point R can be first approximated by a passage of the graph of the apparent productivity of a dispersion flow $P'_x = = f(S_x)$ through the peak to which the values C'_R and S_R correspond. By substituting the values of C'_x and S_x into Eq. (46) for a point downstream from point R, let us find the local value of α'. Repeating these calculations for points $R+2$, $R+3$ . . ., we can find 3-4 values of α', from which to calculate the geometrical mean $\tilde{\alpha}'$.
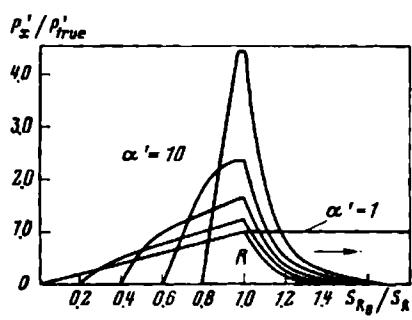
FIG. 18. Graphs of apparent productivity P'_x/P'_{tr} at $\alpha' = 10$ and $\alpha' = 1$ for different values of S_{R_0}/S_R

Given $\tilde{\alpha}'$, it is possible to find the true productivity of a dispersion flow. By solving Eq. (43) with respect to P, we get

$$P = P'_{tr} = \frac{C'_x(S_R - S_{R_0})}{1 - \left(\dfrac{S_{R_0}}{S_x}\right)^{\alpha'}}$$

A multiplication and division of the numerator of the above relationship by S_R, allowing for the fact that $C'_R S_R = P'_R = P'_{max}$, ultimately yields:

$$P'_{tr} = P'_{max}\left[\frac{1 - (S_{R_0}/S_R)}{1 - (S_{R_0}/S_R)^{\alpha'}}\right] = \lambda' P'_{max} \qquad (47)$$

Thus the true productivity of a lithochemical dispersion flow which does not satisfy the condition $P'_x = $ const can be found from the maximum apparent productivity P'_{max} by using a correction factor λ' governed by the local value of α' and the relationship between the catchment areas at points of onset S_{R_0} and discontinuation, S_R, of transport of metal from a slope to the stream bed. A nomogram plotted by the use of Eq. (47) permits the determination of this correction factor $\lambda' < 1.0$ from the established value of α' and the particular proportion between S_{R_0} and S_R. By considering this nomogram (Fig. 19), we can see that, given $S_{R_0} = 0$ or $\alpha' = 1$, we get $\lambda' = 1.0$ and have $P_x = $ const.

The quantitative interpretation of lithochemical dispersion flows by the above method uses microcalculators "Elektronika Б3-18" or programs prepared for "Б3-21" or "MK-46" machines. To interpret dispersion flows by the use of computers Yu.V. Shvarov has prepared a program termed "Potok" (Russian for flow) relying on the determination of the weighed mean sum of the apparent productivity P'_x and "statistical" component of the productivity P''_x mirroring deposition in the stream bed of material washed from a slope in conformity to the relationship

$$P'_{tr} = \beta' P'_x + (1 - \beta') P''_x$$

where β' is a term called a "drift coefficient" and is meant to satisfy the condition $\beta' = 1/\alpha'$.

Given $\beta' = 1.0$, we have an ideal dispersion flow to deal with. At $\beta' = 0$ the dispersion flow in the stream bed repeats the average metal content $\overline{C}_x$ on slopes along gradient lines of the river plain relief connecting

FIG. 19. Nomogram for estimation of λ' from values of α' and S_{R_0}/S_R

sampling points with the divide line. The statistical component is determined by the value of the integral $P''_x = \int\limits_0^S (C'_x - C'_0)\, dS$ monotonically increasing as the stream outlet is being approached. Since the apparent productivity downstream from point P is monotonically diminishing, it is possible to find β' and P'_{tr} by referring to the condition $P'_{tr} = \text{const}$. To substantiate these estimates by using the data on all sampling points suggesting anomalous amounts of metal, the "Potok" program carries out an approximation of average values on slopes by referring to the normal distribution, rather than the rectangular, used previously. The determination of the parameters of this distribution, i.e. $\overline{C}_{max}$, σ and coordinates of its midpoint S' is made concurrently with that of β' and P'_{tr} by the least squares technique and the relevant data are printed. Figure 20 is an illustration of what has been said above. Both the methods of interpretation, "manual" and computer-assisted, yield practically identical results and are based on an assumption that over the entire interval of the stream bed from $x = R_0$ to $x = R$ secondary dispersion aureoles on slopes make up one common anomaly from which ore element is supplied to the stream bed, there being no other anomalies outside this interval. This does not rule out the presence of
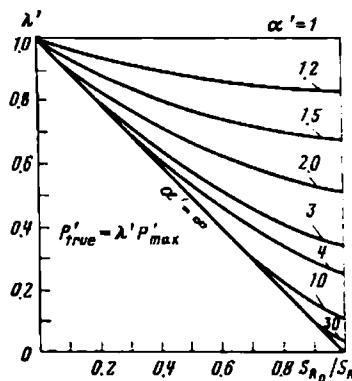
other ore bodies in the catchment area of the particular stream bed on the condition that downstream from point R the ore element content in the alluvium is diminishing to attain the background value and it becomes feasible to consider it separately. In practical prospecting this condition is often violated, and within one stream bed there occur several anomalies that are superimposed to one extent or another. Figure 21 illustrates examples of this kind. If throughout the length of a stream bed $\alpha' = 1.0$ and dispersion flows satisfy the

condition $P'_i = \text{const}$, the sum total of all separate anomalies is determined from the farthest downstream value of its consistent values. As to the productivity of each individual anomaly, it is determined as a difference of two adjacent consistent values: $(P'_i)_{tr} = (P'_i)_{obs} - (P'_{i-1})_{obs}$. Given values of $\alpha' > 1.0$ graphs of dispersion flows associated with closely located targets are essentially complicated. Two or more close anomalies the ore element contents in which at $\alpha' > 1.0$ remain anomalous can be interpreted by the use of the most elementary counting techniques. To do this, the productivity of

FIG. 20. Concerning computerized interpretation of dispersion flows. After Yu.V. Shvarov

the flow due to the effect of the first (from the watershed apex) anomaly should be subtracted from $P'_{max\,2}$ or

$$P'_{tr2} = \lambda'_2 \, [P'_{R2} = P'_{R1} \, (S_{R1}/S_{R2})^{\alpha'_1 - 1}] \qquad (48)$$

The subscripts 1, 2 mean that the particular quantity belongs, respectively, to the first or second anomaly. In like manner three or more close anomalies within one stream bed can be interpreted. The sum of all true, including consistent, productivities of the dispersion flows in the particular stream bed and the adjacent ones yield the net productivity of an ore deposit $\sum\limits_{i=1}^{m} P'_i$ entering into Eq. (39) used to estimate prospective metal reserves.

Sec. 2.4. Procedures of Prospecting Surveys

The search for ore deposits from their lithochemical dispersion flows at the first stage of geochemical prospecting is conducted by continuous sampling of the alluvium of the particular mountainous area drainage system. Samples are collected from the alluvial sedi-

FIG. 21. Calculation graphs for apparent productivity of dispersion flows for different distances between orebodies I and II at $\alpha' = 1.0$; 3.0 and 10. After A.P. Polkvoi

Arrows show the direction of runoff

ments in the dry areas of the floodplain at a depth of 10-15 cm, less often from the water. It is the sandy and clayey fraction of the alluvium that is sampled, in its absence, the silty and clayey fraction, and, in the absence of the latter, the gravel and gruss fraction is sampled, that is, silt that forms the solid load under the local conditions. Frequent change of material to be sampled should be avoided since it impairs the interpretation of the analytical data and enhances the dispersion of the background. The mass of a sample should be 150-200 g which calls for removal of coarse detrital material. The same objective is served by the subsequent screening of an aerial dry assay.

What is the best fraction to be screened for further analysis poses a problem. Some ore elements occurring as heavy stable minerals (e.g. SnO_2) can enrich coarse-grained alluvial fractions, others largely concentrate in silt and clay fractions, often in a nonmineral form (e.g. Mo, U). The enrichment of a fraction by an ore element does not suggest that it is more advantageous for prospecting, for it may be followed by a concurrent increase in the background values and standard factor, i.e. *a decrease of the contrast* of geochemical anomalies. Moreover, one and the same ore element in the immediate vicinity to an ore deposit enriches coarse fractions of the alluvium, and with increasing the distance from the primary ore deposit, the contrast of anomalies enhances in fine fractions. Since it is impossible to pinpoint the orebody during prospecting operations in advance, no preference can be given to any of the fractions. That is the reason why a different procedure is to be recommended: it is best to screen for further analysis such a small fraction of field samples which presents no problem to extract and 50 g of whose output is ensured without increasing the mass of the initial samples. Lithochemical prospecting referred to supergene dispersion aureoles and flows generally uses for analysis 1.0 or 0.5 mm diameter fractions. To decide on a sampling grid calls for a more detailed consideration [1]

Lithochemical surveys referred to dispersion flows are generally conducted in areas the geological setting of which has been inadequately studied, which are poorly developed economically and often are not readily accessible. Under such economic and geological conditions the first stage of orientation prospecting consists in the discovery solely of large deposits. Concurrent search for small deposits should be warned against. Sampling of alluvial and proluvial sediments of sporadic streams with minor catchment areas $(S_x \rightarrow 0)$ may reveal these small deposits and occurrences of little economic importance which is out of line of geochemical exploration and impairs the efficacy of operations. Clearly, the spacing of sampling points should be governed by the minimum dimensions of orebodies likely to be discovered. At the early stage of prospecting for deposits that contain "reserves that can be readily proved" (see Fig. 10a),

their dimensions can be inferred from the areal productivity of dispersion aureoles and flows P, P', proportional to the productivity of the primary ore deposit P_p m²% at the level of the modern ground surface. If the condition $C_x \geqslant C_A = C_0 \varepsilon^3$ is satisfied, it is possible to discover an orebody. The maximum ore element content in a dispersion flow is in the most common case referred to point R below which anomalous content values only decrease. Given that

$$C'_{max} \geqslant C'_s \varepsilon^3 = (P/S_R) + C'_0, \text{ we have}$$

$$S_R \leqslant \frac{P}{C'_s(\varepsilon^3 - 1)} = S_{crit} \qquad (49)$$

This relationship corresponding to an idealized dispersion flow, makes it possible to determine the maximum catchment area S_{crit} at which testing of alluvial deposits will discover an orebody with a specified productivity of the secondary dispersion aureole P m²%. An orebody with the same productivity located within an area $S_x >$ $> S_{crit}$ will not be revealed by lithochemical surveys of its dispersion flows, whereas orebodies with $P > P_{crit}$ will be pinpointed under identical conditions. By taking into account a decrease of S_x as the watershed apices are approached, the condition $S_{min} \leqslant S_{crit}$ at a specified P_{min} determines whether it is possible to discontinue sampling as a watershed is being approached without impairing the efficiency of lithochemical prospecting operations. At points where sampling is discontinued at $S_x \leqslant S_{min}$ it is usual to collect two samples spaced at intervals 20-30 m. In a pedestrian survey samples are generally collected with the spacing 500-1 000 m in view of the fact that the length of traverses is what generally makes these operations labour-consuming. Figure 22 illustrates a reasonable spacing of sampling points for 1 : 500 000 scale surveys. Here $S_{min} \leqslant 10$ km², $C'_0 = 0.1$ ppm, $\varepsilon = 1.44$, and $C'_A = 0.3$ ppm. No samples are taken in order II river mouths, order I rivers are sampled only where they flow into order III and senior-order rivers, the spacing being 500 m. The given area contains two orebodies of minor economical importance each of which displays a productivity of the secondary dispersion aureole $P_{min} = 400$ m²%. Over an area 100 km² representing a segment of the total area being surveyed, 22 singular and 9 double samples have been collected assigned sequence numbers 1-40 which corresponds to an average density 1 sample per 2.5 km², i.e. a design sampling grid is 5×0.5 km.

Lithochemical surveys on this scale reveal the orebody A. Its secondary dispersion auereoles are almost* equally distributed between two catchment areas of orders I-II, respectively, $S_{28,29} \approx 5$ km² and $S_{33,34} \approx 10$ km². As a result, the element content in samples 28 and 29 will be 0.5 ppm, in samples 33 and 34, 0.3 ppm. In addition, the metal content in eight samples (21, 22, 25 to 27 and 30

to 32) will be 0.2-0.25 ppm, i.e. anomalous, referred to a criterion $C_0 \varepsilon^{3/\sqrt{m}}$. The orebody B that happens to occur in order IV stream basin fails to be discovered by surveys under conditions of an ideal dispersion flow. Point R in this case corresponds to a catchment area $S_R = S_x = 74$ km^2 > $S_{crit} = 20$ km^2. The maximum ore content is $C'_{max} = C_R = 0.15$ ppm < C_A. Within the area shown in Fig.22
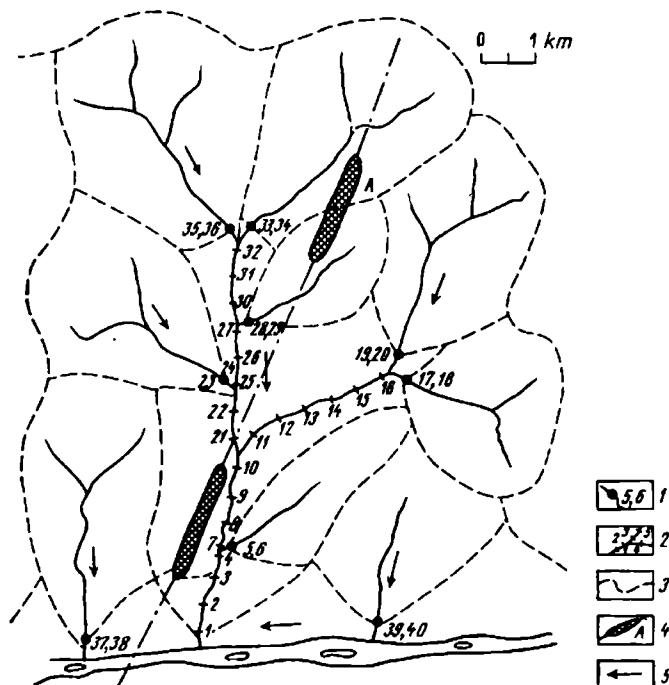

FIG. 22. Example of location of sampling points for 1/500 000 scale surveys.
Sampling points: 1 — double; 2 — single; 3 — watersheds; 4 — orebodies; 5 — direction of runoff

ΣS_{min} takes roughly 75 % of the total area of the given segment. Clearly, further sampling as the watershed is being approached would serve no purpose. These expected results of a lithochemical survey were inferred from the mechanisms of the formation of idealized dispersion flows. The mechanisms, however, may vary in actual conditions. The disturbance of the condition $P'_x = $ const, which makes it difficult to interpret dispersion flows, on the other hand, plays a positive role enlarging the efficacy of the lithochemical survey. This is illustrated by three curves $C'_x = f (S_x)$ shown in Fig. 23. At values of $\alpha' = 1.0$ when the formation of a dispersion flow is

approximated by an idealized model, an orebody whose productiv-
ity is 400 m²% of Ag (or Hg), given $S_R = 50$ km², will remain un-
discovered. This is because $S_{crit} = 20$ km², and the ore element
content values remain lower than C'_A (shown by a dashed line in
Fig. 23) at all sampling points. Even given $\alpha' = 3$ in two samples and
$\alpha' = 10$ in seven samples, the element content shows anomalous val-
ues, thus permitting a reliable identification of the orebody. By
summing up these data and using Eq. (47), we establish that in real
dispersion flows with S_{crit} or a specified C_R the metal content ($C'_{max} - C'_0$) increased by a factor of $1/\lambda'$ compared with ideal conditions.
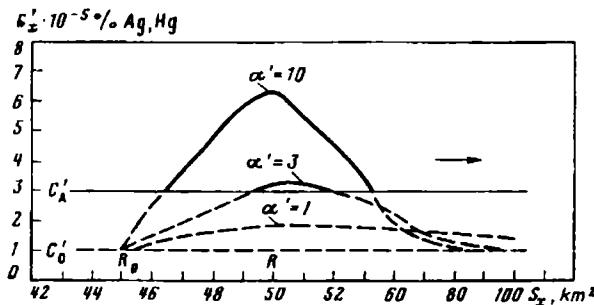
FIG. 23. Graphs for pinpointing targets of search at $S_x > S_{crit}$ and $\alpha' \geqslant 3$,
$Q_{100} = 1\ 000$ t, $P' = 400$ m²%, $S_{crit} = 20$ km², k' and $k = 1$.
Arrow shows the direction of runoff

Depending on the local values of α' and S_{R_0}/S_R ratios this increase
may be 20-, 30- and even 50-fold which appreciably enhances the
efficacy of lithochemical surveys referred to dispersion flows. From
Fig. 22, we can see that the orebody B that defies identification is an
idealized dispersion flow, given that $S_{R_0}/S_R = 0.88$, can be reliably
revealed from the anomalous metal content values starting from
$\alpha' \geqslant 4.7$. At $k' > 1.0$ (e.g. Au, Sn), added reserves appear, at $k' < 1.0$
the efficacy of prospecting is deteriorating. Thus it should be consid-
ered reasonable to use the spacing 0.5 to 1.0 km when samples are
to be collected from stream beds of senior order rivers with catch-
ment basins of a few hundred square km in area. So we do not have
to augment lithochemical surveys of dispersion flows, before their
results have been obtained, by profile samplings of eluvio-deluvial
material on the adjacent slopes.

The local values of k' are determined at sections of the discovered
ore element dispersion flows to be followed by a lithochemical sur-
vey of secondary dispersion aureoles on a 1 : 100 000 or larger scale.
To calculate the particular values of k' from the data of the surveys,
Eq. (16) is used to find the areal productivities of the portion of sec-
ondary dispersion aureoles that, by virtue of slope denudation con-

ditions, suggest definite sites for collecting samples from stream sediments. By using Eq. (35) for the same sampling points we calculate the productivity of dispersion flows having determined the catchment area S_x from topographic maps or aerial photographs. The values of k' are calculated accurate to the second decimal place as a quotient of the division of P' by P. The geometrical mean $\tilde{k}'$ is determined for the established n values of k' corresponding to similar conditions, and from the value of the k'_{max}/k'_{min} ratio we calculate the standard factor ε governing the confidence levels of the estimated $\sim k' \cdot \varepsilon^{\pm 1}$, where $\varepsilon = $ antlog of $s_{\log}/\sqrt{n}$. The statistic distribution of k' is approximated by the lognormal distribution owing to the fact that the mean of two equally probable values of the proportionality factor 2.0 and 0.5 is $1.0 = \sqrt{2 \times 0.5}$, rather than $1.25 = \dfrac{2 + 0.5}{2}$.

Figure 24 illustrates determinations of $\tilde{k}'$ for Pb dispersion flows under Alpine conditions of the Ugam ridge, South Kazakhstan. The total geometrical mean for Pb found for 81 determinations in this region proved fairly close to 1.0. Particular values of k' for definite ore regions are presented in Table 11.

TABLE 11

k' Values

Nos.[*]	Ore element	Number of determinations	Estimate	Nos.[*]	Ore element	Number of determinations	Estimate
1	Pb	7	$1.21 \times 1.39^{\pm 1}$	11	Ag	26	$0.88 \times 1.63^{\pm 1}$
2	Ag	8	$0.16 \times 1.33^{\pm 1}$	12	Sn	19	$1.44 \times 1.98^{\pm 1}$
3	Cu	10	$0.97 \times 1.09^{\pm 1}$	13	Bi	18	$1.29 \times 1.60^{\pm 1}$
4	Sn	6	$1.46 \times 1.37^{\pm 1}$	14	As	21	$1.17 \times 1.59^{\pm 1}$
5	Pb	11	$1.61 \times 1.18^{\pm 1}$	15	Pb	8	$1.11 \times 1.10^{\pm 1}$
6	Zn	9	$0.86 \times 1.31^{\pm 1}$	16	Zn	6	$1.12 \times 1.41^{\pm 1}$
7	Mo	10	$2.06 \times 1.08^{\pm 1}$	17	Ag	5	$1.30 \times 1.26^{\pm 1}$
8	U	7	$1.13 \times 1.12^{\pm 1}$	18	Mo	4	$2.23 \times 1.15^{\pm 1}$
9	Pb	25	$1.06 \times 1.74^{\pm 1}$	19	As	3	$1.47 \times 1.21^{\pm 1}$
10	Zn	25	$2.75 \times 1.71^{\pm 1}$	20	Ba	2	$3.77 \times 1.15^{\pm 1}$

* Data submitted: 1-4 by A. D. Ananchenko relating to the Northern Kamchatka Region; 5-8 by A. N. Bogolyubov relating to Soviet Middle Asia; 9-14 by V. P. Borodin relating to the Omsukchan district of the Magadan Region; 15-20 by S. A. Milyaev relating to mountainous areas of Kazakhstan.

If there is an extensive aqueous (hydrochemical) migration of chemical elements followed by abrupt changes in the local conditions, these may be stream deposited at geochemical barriers. The resultant secondary (supergene) concentrations of elements with values
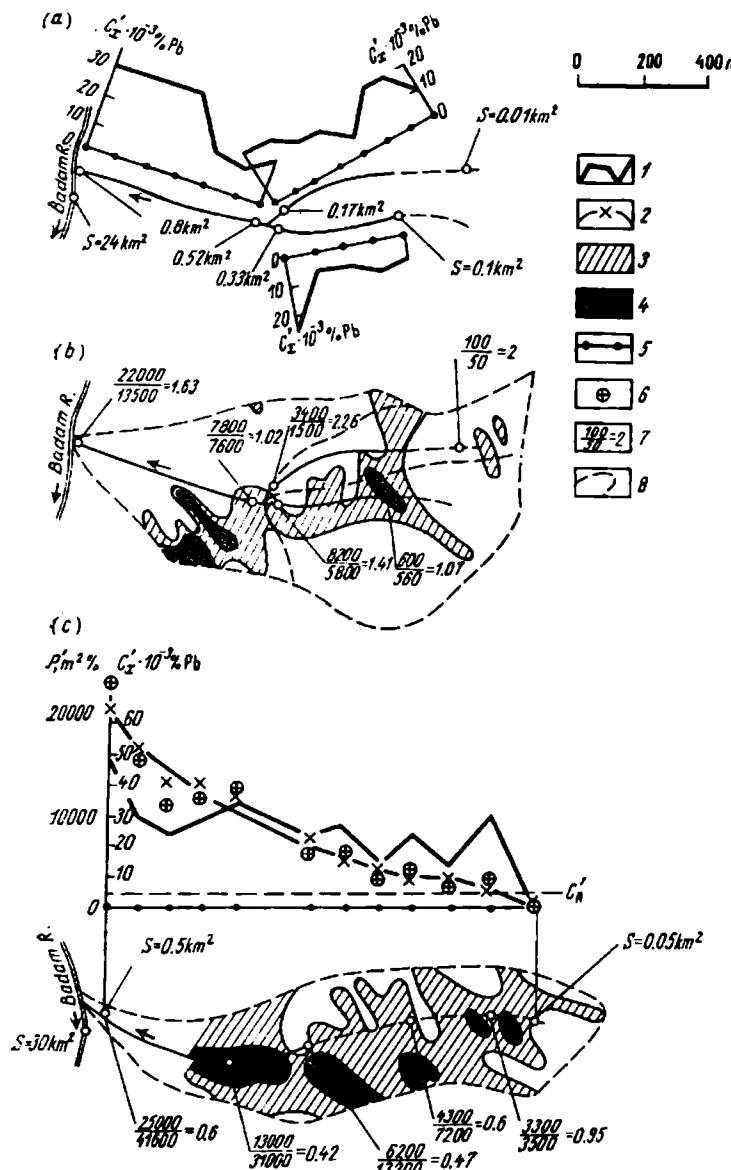
FIG. 24. Concerning estimation of proportionality coefficients k' between Pb content in dispersion flows and aureoles for water streams Sai No. 13 (a, b) and Sai No. 10 (c). After A.P. Solovov and N.Ya. Kunin.

Graphs: 1 — Pb contents; 2 — averaged values of P'_x. Dispersion aureoles: 3 — Pb $\geqslant 0.02$ %; 4 — Pb $\geqslant 0.1$ %; 5 — dispersion flow sampling points; 6 — calculated values of P'_x; 7 — $P'/P = k'$; 8 — contour of denudation basin

of $k' \gg 1.0$ may inhibit quantitative interpretation of dispersion flows.

Their formation at an evaporation barrier has been recorded for Sr, B, F, sometimes Mo; at a reduction barrier, for U and Mo. In the limit, supergene concentrations may be of economic importance, assuming the meaning of exogenic deposits of minerals.

Another group of ore elements whose dispersion flows may manifest the values of $k' \geqslant 1.0$ is made up by Au, Pt and other elements represented by weathering-resistant heavy minerals, such as cassiterite, monazite, columbite, tantalite, ilmenite, rutile, in part, tungstenite. These minerals, exhibiting a pronounced density and mechanical strength, may accumulate at a gravitational barrier forming in the stream sediments alluvial placers showing a large and very much variable coefficient of enrichment. The pronounced density $(d = 19.3 \ g/cm^3)$ and the involved mechanism of hydraulic sorting out prevent the local values of k' for Au in each particular stream from being accurately predicted. Therefore Eq. (39) is not being currently used for estimating reserves of gold ore deposits. Lithochemical platinum dispersion flows $(d = 21.4 \ g/cm^3)$ have not as yet been adequately studied. For most of remaining ore elements occurring in mountainous conditions, adequate data lacking, rough estimates may assume $k' = 1.0$ taking actual values of the proportionality coefficient to be unlikely to affect the expected figures. With weakly erosion-dissected relief approaching conditions of a plain it becomes doubtful whether dispersion flows can be interpreted in quantitative terms.

The methods of lithochemical prospecting for ore deposits in regions with a surficial layer of moderate thickness made up of continuous moraine sediments including appreciable areas of the Kola Peninsula, Karelia, Finland and Canadian shield should be dealt with separately. As has been shown by practice, under such conditions glacial dispersion flows related to ore deposits can be discovered.

Dispersion trains are particularly characteristic of the glacial fan of the ore boulder materials by the mapping of which a number of ore deposits were discovered in the past in Finland. In these instances there is no doubt as to the residual (mechanical) nature of lithochemical anomalies in the moraine. There are other cases, as N. F. Maiorov [20] believes, where secondary dispersion aureoles and flows associated with ore deposits involve salt superposition. Lithochemical anomalies in the moraine material transported at the base of a valley glacier approximate the most closely dispersion flows. Typical lithochemical dispersion flows may form in fluvioglacial sediments in interglaciation periods or in stream sediments of a modern drainage system dissecting stream bottom moraine over vast areas of glacial plains.

Secondary Lithochemical Dispersion Aureoles from Ore Deposits

Sec. 3.1. Weathering and Denudation

Rocks that compose the earth's crustal layers are subject to denudation following weathering. This causes loose (disperse) materials in the supergene zone to be formed whose physical properties differ very much from those of the parent bed rock.

Of the principal rock-forming minerals, high resistance to chemical weathering is only exhibited by quartz SiO_2. Chemical weathering of primary alumo- and ferrosilicates is amply revealed by the fact that they decompose to form secondary argillaceous materials, oxides and hydrooxides. Primary alumosilicate, as a result of hydrolysis, loses metal cations (K, Na, Ca, Mg...) that are dissolved and transported as carbonates, halides, sulphates and other salts. This stage of weathering gives rise to hydromicas and argillaceous minerals of the montmorillonite group $Al_4Si_8O_{18}|OH]_{12} \times nH_2O$ that are relatively resistant to the alkaline and neutral environment (pH $\geqslant$ 7). As bases are leached and the acidity of the medium increases (pH $<$ $<$ 7), montmorillonite transforms to halloysite, and the latter, on dehydration, to kaolinite $Al_4Si_4O_{10}[OH]_8$, the end products of which are alumina $Al(OH)_3$ and silica. Colloidal silica liberated in these reactions is then washed out, in part, by fluids, and in part is sedimented as gels of a composition $SiO_2 \times nH_2O$. Following dehydration and crystallization, silicic acid gel converts to common quartz. Secondary quartz is as stable chemically as that in igneous rocks. A minor fraction of alumina is carried away as solution, and the major part is precipitated as gels $Al_2O_3 \times nH_2O$. Weathering of ferrosilicates eventually produces silica and, respectively, resistant ferrum hydroxides $Fe_2O_3 \times nH_2O$—goethite and limonite. A fraction of colloidal ferrum hydroxide remains in solution reacting to form different mineral and organic compounds or is carried out by drainage waters. The above pattern of chemical decomposition of silicates suggests a general trend of the process which develops to the full extent or in part, depending on the physical and chemical environment. A very long geological time period is necessary for chemical weathering to be completed, therefore appreciable quantities of unstable primary rock-forming and secondary clayey minerals are often transported to the base level of erosion before they reduce to free oxides.

B.B. Polynov has isolated four stages of weathering that are typical of the time-dependent continuous process of hypergenesis. *The first stage* involves the predominant role of physical agents of weathering that change parent rocks of a massif to the clastic state forming coarse- and fine-grained detrital materials. Under inclement environmental conditions and active denudation modern weathering sometimes terminates at this early stage. *The second stage* involves the alkaline reaction of the environment due to leaching of bases during hydrolysis of minerals. It is at this stage that secondary minerals form following oxidation, hydratation, hydrolysis and carbonization of the primary minerals. Of secondary aluminosilicates, minerals of the montmorillonite group and nontronite are dominant at this stage. The relative abundance of calcium in rocks causes calcium carbonate often forming crust on massive rock fragments to be accumulated in the products of weathering. B.B. Polynov describes this stage as calcified or siallitic alkali saturated crust. It finds the largest distribution in temperate zones during weathering of igneous and metamorphic rocks. Modern loose surficial materials of slopes in mountainous country are often of this type.

The third stage, that of residual unsaturated siallitic weathering crust is characterized by further removal of alkaline and alkaline earth elements from the products of weathering which results in the acidity of the medium. Under such conditions halloysite and kaolinite dominate among secondary aluminosilicates. This weathering stage develops under conditions of retarded denudation and relatively greater wetting. *The fourth stage* involves the formation of a residual allitic weathering crust typified by the accumulation of silicon, iron and aluminium oxides. Its development is conditioned by intensive chemical decomposition combined with slow denudation in a hot and humid environment. Currently the development of an allitic residuum on the territory occupied by the USSR does not occur. It is only traces of it that can be revealed at localities where ancient-origin residuum formed in past environments has been preserved. The allitic type of weathering is best represented by the red earths of the humid subtropical area in Transcaucasia (vicinity of the town Batumi) which owe their colouration to ferrum hydroxides accumulated therein.

What is by far the most important result of weathering is the formation in the supergene zone of colloidal suspensions, i.e. particles 1×10^{-1} to 1×10^{-3} μm in diameter. Such dimensions unusually increase their specific area. The material thus attains new properties due to the electrical charge of the particles and the action of surficial forces. Colloidal suspensions of the supergene zone form in the processes by which the parent rocks are fragmented during weathering or in chemical reactions occurring in the zone of weathering or during decay of organic remnants. The electrical charge of colloidal

particles is what determines sorption of the oppositely charged ions from the solution medium. In the aqueous medium typical of the supergene zone, clay and organic colloids are negatively charged and sorb metal cations; identical properties are exhibited by SiO_2 and MnO_2 colloids. $Fe(OH)_3$ and $Al(OH)_3$ colloids are positively charged. Clay minerals display different absorption capacity, the greatest being that of montmorillonites and the smallest in kaolinites.

Once formed, a layer of weathered rocks facilitates further denudation concurrently rendering it more difficult for weathering agents to reach the unaltered bed rocks. Removal of decomposed and disintegrated material by denudation enhances the weathering, which, in turn, intensifies denudation. As a result, there is a mobile equilibrium between weathering and denudation governing the thickness of the regolith in positive relief forms. The mobile, or dynamic, equilibrium does not rule out forward movement which may cause the equilibrium to be shifted in one direction or another. Should denudation play the dominant role, then the thickness, h, of modern weathering products diminishes under new conditions of equilibrium. The latter will be attained at greater values of h under conditions of retarded denudation and, consequently, lengthier weathering.

The time T, indicating the period taken by an elementary layer of friable formations at a depth $z \leqslant h$ from the ground surface to be found in the zone of weathering will be determined from this linear relationship

$$T = \frac{h-z}{\Delta h} \tag{50}$$

The upper horizon of the loose superficial material ($z = 0$) that was the first to be attacked by agents of weathering will be participating in the process for the longest time period

$$T_0 = T_{max} = \frac{h}{\Delta h} \tag{51}$$

A lower horizon at a depth h, that is at a boundary of intact, unaltered rocks will correspond to $T_h = 0$, since weathering agents have just penetrated to this depth. If the process is stable, the observed pattern is not time-dependent, and T_z is a parameter characterizing the local conditions. It is possible to approximately determine the time period T_0 from the onset of weathering of a random layer of the bedrock till the moment denudation agents remove its weathering products. Assuming, e.g. that the average thickness of the denudation layer of a mountain slope is $\Delta h = 0.25$ mm per year and the thickness of clay and crushed rock materials typical for these conditions is $h = 1.5$ m, we have $T_0 = \frac{h}{\Delta h} = 6000$ years. By way of comparison, according to the data of V.P. Petrov, it

took about 0.5-2.0 million years for the ancient-origin kaolinite residuum to form in the Urals which is characteristic for smooth relief features. The fact that only fragmented and coarse skeletal soils occur on a mountain slope suggests the high rate of denudation.

Weathering and denudation give rise to loose materials of various types and varying in thickness at the expense of the underlying parent rocks. *Loose* (or denser) *sediments*, transported products of weathering overlying the bed rock at lower areas are of a different origin. The effectiveness of lithochemical exploration for ore deposits
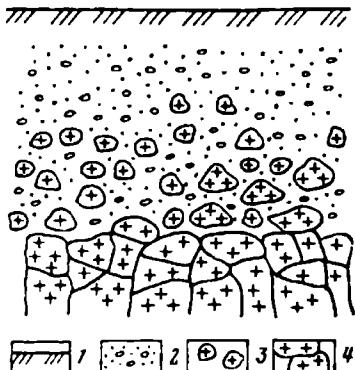
FIG. 25. Vertical cross section of eluvium:

1 — soil and vegetation cover; *2* — sandy clayey assemblages; *3* — bedrock debris; *4* — bedrock
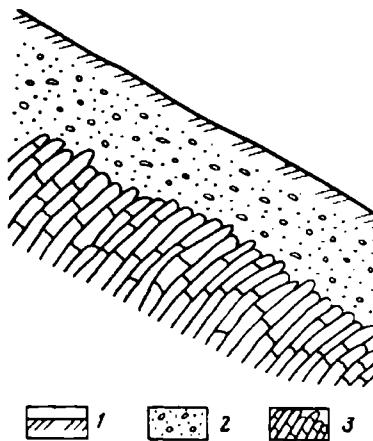
FIG. 26. Vertical cross section of eluvial-deluvium:

1 — soil and vegetation cover; *2* — sandy clayey assemblages with crushed rocks; *3* — bedrock at initial stage of weathering

by pinpointing their secondary dispersion aureoles is largely governed by the genesis of loose formations and their relations with the substratum.

Eluvium, disintegrated material of weathering accumulated *in situ* forms under conditions of smooth relief at an early stage of weathering. The number of detrital particles will continuously increase and their average diameter diminish since the moment the first fragment forms on the surface of a dense rock which is being attacked by weathering. This process is irreversible, so the eluvial grains are generally smaller, the closer the earth surface. A vertical section of eluvium shows it to gradually change to a dense bedrock (Fig. 25).

The same mechanism is generally valid for a gradual disintegration and fragmentation of an initially solid orebody. Small-grained material falling between coarse detrital rock fragments and being transported by meteoric water or wind action may sometimes be located

some distance from the ground surface. In cold and temperate zones eluvium is usually only a few metres in thickness, and in hot and humid environment may attain 100 m. The composition of eluvium mirrors that of the parent rocks and whether these include mineralization whatever form it may have as a result of chemical processes and biogenic agents.

Deluvium (talus) is loose material of any petrographic composition covering mountain slopes and representing weathering products of the bed rocks transported by gravity and atmospheric precipitation. The layer of deluvium which is continuous at the foot of a slope reaches the watershed to mix with eluvium which is of a similar origin. As a result, friable loose material covers the entire area by a mildly undulating eluvio-deluvium layer. When conducting lithochemical exploration for ore deposits by locating their secondary dispersion aureoles we typically deal with these very eluvio-deluvium materials, products of weathering that have been moved to a minor distance whose composition and location distinctly suggest the parent bedrock. The thickness of eluvio-deluvium materials is largely governed by the denudation rate and varies in the range from 0.5-2 to 10-12 m, seldom more. The composition of the eluvio-deluvial formations at a particular point will agree to that of the bedrock located upslope. Referring to a vertical section, the eluvio-deluvial materials change with depth for eluvium which, in turn, passes to a solid bedrock (Fig. 26). The solifluction formations that develop in permafrost conditions and Arctic environment should be referred to a separate genetic type. Proluvial, alluvial and glacial deposits that overlie the parent bedrock are intricately connected with this latter in terms of composition and character. By contrast, various aeolian, lacustrine, marine and volcanic rocks which form when denudation is succeeded by sedimentation have no immediate genetic connection to the undermass. In favourable conditions, however, secondary dispersion aureoles of ore deposits occurring in the basement rocks may crop out and reveal themselves in the overlying transported sediments of minor thickness due to epigenetic processes to be considered below.

Sec. 3.2. Classification of Secondary Dispersion Aureoles

Weathering is continuously producing and denudation is continuously varying lithochemical dispersion aureoles of ore deposits, orebodies or primary halos crop out at the erosional surface (see Fig. 4, Levels *B-D*). This process, tending to be regular, is responsible for the formation of secondary dispersion aureoles from ore deposits as stable geological features of the supergene zone that obey quite definite mechanisms. Forming, as it does, local anomalies of a supergene dispersion field in regions of intensive denudation, this

principal process of the formation of secondary lithochemical dispersion aureoles is not unique. The diversification and complicated nature of dispersion processes call for a classification of dispersion aureoles. By identifying separate elementary events underlying an involved process, it is possible to study all facets of it in great detail. The genesis, morphology and quantitative characteristics typical of one kind of secondary dispersion aureoles are what determines their importance in terms of prospecting and geological interpretation. N.I. Safronov proposed a classification of secondary dispersion aureoles as far back as 1936 [29], which, for minor alterations, holds true up to now.

According to *the phase state* secondary dispersion aureoles are divided into mechanical, salt and gaseous.

In *a mechanical dispersion aureole* the mineral components are available in solid phase—primary or secondary minerals and ore fragments stable in the supergene zone. A mechanical dispersion aureole results from the disintegration of an orebody, separation of ore minerals and fragments from the monolith and their mobility. The principal horizons where mechanical dispersion aureoles form are modern eluvio-deluvium materials and ancient residuum of the enclosing rocks. Mechanical dispersion aureoles are formed by most ore deposits, predominantly, ones of gold, platinum, cassiterite, chromite and a number of other minerals.

The mineral ingredients of an ore deposit are available in *a salt dispersion aureole* as solutions or ore fluids intricately linked to rocks. Secondary salt aureoles are formed by the movement, diffusion, capillary rise and evaporation of mineralized waters resulting from the dissolution of ore minerals, generally at the stage of supergene alteration. A salt dispersion, contributing to the formation of composite (mechanical and salt) secondary aureoles in the eluviodeluvium formations, may develop as early as the stage of blind occurrence of an orebody and primary halos (see Fig. 4, level *A*) as the subsurface waters attack the upper horizons of the mineralization.

In favourable conditions, a salt dispersion may penetrate into the overlying transported sediments cover. Salt aureoles ingradients may be assimilated by the root systems of plants to form biogeochemical aureoles in the growing vegetation. The ultimate mineralization of the decayed vegetative material forms a biogenic component of the complex lithochemical dispersion aureole. Salt dispersion aureoles are, in particular, formed by copperpyrite and fluorspar deposits and, to one degree or another, all other types of ore deposits.

The gaseous dispersion aureoles are formed by the diffusion and effusion of the gaseous constituents coming through the overburden mass to the ground surface. Gaseous dispersion aureoles are typically related to radioactive ore deposits and develop independently of

weathering or of the position of the denudation surface with respect to the lode. They result from the spontaneous decay of elements emanating radon and thoron. The presence of gaseous dispersion aureoles has been proved for mercury deposits which is due to the pronounced elasticity of mercury vapours even at general temperatures at the earth surface [9]. The fact that vapours of lead, copper, zinc, tin, or any other metals participate to one degree or another in supergene dispersions of ore deposits as atomic gas or, e.g. as more volatile haloid compounds is a matter of common knowledge, but seems to play a minor role. Methods for the detection of gaseous aureoles of these ore elements are still under elaboration. Gaseous components, subject to adsorption and occlusion by the surfaces of the grains forming the unconsolidated overburden material, contribute to the lithochemical dispersion aureole. Thus, secondary lithochemical dispersion aureoles from ore elements predominantly form in a solid phase, salt dispersion is of less importance, and gaseous dispersion is of the least value. What follows considers in more detail only secondary mechanical and salt dispersion aureoles. Gaseous dispersion halos are dealt with in Chapter 5 which outlines methods of atmochemical prospecting.

Secondary aureoles in the modern eluvio-deluvium or ancient weathering crust formed at the expense of the intervals of an orebody or its primary halo that existed in a vertical section of the bedrock before weathering are called *residual dispersion aureoles*. By contrast, there are *superimposed aureoles* in whose contours no primary ore mineralization occurred before the onset of secondary dispersion.

The most essential feature of the secondary residual dispersion aureoles is proportional to M, m%, and areal P, m^2%, productivities to the identical parameters of the primary mineralization M_p, P_p, expressed by Eqs. (18) and (19). The proportionality factor $k \gtrless 1.0$ entering into these relations and governed by the local geochemical environments and properties of the particular ore element, is known for these aureoles as a coefficient of the residual productivity.

Depending on the accessibility, we distinguish *outcropping aureoles*, i.e. ones that are exposed to the modern ground surface and *concealed dispersion aureoles* to be located some depth from the surface. Concealed aureoles may be due to the wash out of mobile ore elements by atmospheric precipitation from the upper eluvial horizons or to the change in the base level following the development of a residual dispersion aureole that has given rise to the formation of a transported cover and caused the aureole to be buried. The presence of this cover allochthonous to the country rocks and their weathering crusts may, in a particular case, fail to prevent diffusional, sorptional, evaporational and/or biogeochemic accumulation of ore elements at the ground surface and may cause an outcropping superimposed lithochemical aureole to be formed (Fig. 27). Unlike the first two

classification features the referring of a dispersion aureole to a concealed type has not a genetic but only a tentative technical meaning. When the list of the chemical elements to be determined is to be reviewed, methods of sample analysis or mathematical handling of the data obtained are to be improved, any "concealed" dispersion aureole may be classified as an "outcropping" halo. That is why a more rigorous definition of the term "a concealed dispersion aureole" would call upon us to point out that it defies discovery at the ground
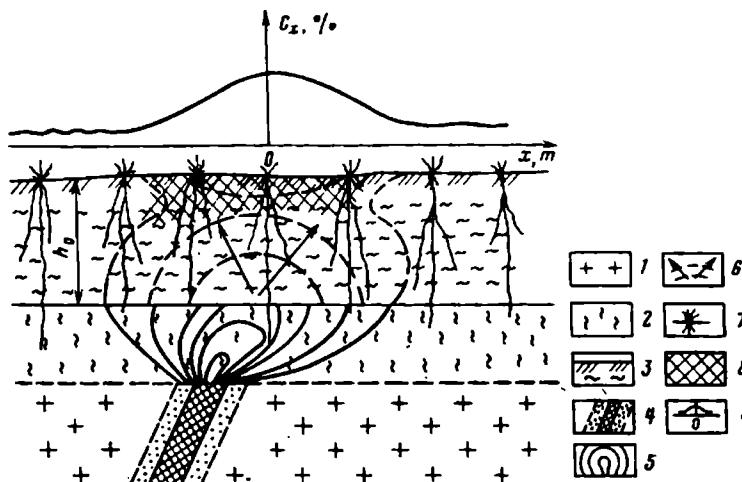
FIG. 27. Diagram showing origination of an superimposed outcropping lithochemical dispersion   aureole:

1 — enclosing rocks; 2 — ancient residuum; 3 — allochthonous sediments with thickness h_a; 4 — orebody and its primary aureole; 5 — concealed secondary residual dispersion aureole; 6 — secondary superimposed dispersion aureole (arrows show direction of mineral component diffusion); 7 — plants capable to form a biogenic component of superimposed dispersion aureole; 8 — horizons of possible evaporational, sorptional and biogenic accumulation of ore elements; 9 — graph of results of terrestrial lithochemical survey

surface by "the use of current techniques". Each of the above classification features characterizes the principal mechanisms of the formation of secondary dispersion aureoles in a particular region and different combinations of these features determine what possible type they belong to. The classification is based on features determining the genetic type of the aureole (residual, superimposed) and its accessibility to observations and also some additional characteristics pointing to their origin (diffusional, leached etc.) or position relative to the primary mineralization. In so doing, it is *a priori* assumed that lithochemical dispersion aureoles form involving solid, soluble and gaseous components that participate jointly or separately, and the role of each phase is determined to describe one type or another. The features characteristic of the aureole type are

studied at the uppermost horizon where it reveals itself. The outcropping aureoles are studied at the earth's surface, and concealed ones at the minimum depth from the ground surface where they are well developed. In geochemical exploration this level is known as a "representative prospecting horizon".

A manual for conducting geochemical prospecting for ore deposits outlines 13 types of lithochemical dispersion aureoles as the most important for geochemical exploration [17]. Some of these are described as "not studied", others are grouped together. Clearly, in terms of morphological properties and relations to relief, the dispersion aureoles may differ infinitely for their characteristics. Yet there are, in fact, not so many types of secondary dispersion aureoles to be dealt with in theoretical or practical terms of geochemical exploration. What follows presents, with some abridgements and additions, seven types of dispersion aureoles (Fig. 28) described in an earlier manual (1965). I-IV type aureoles are outcropping ones, II-IV aureoles being superimposed, and III-IV patterns superimposed accumulated ones. V-VII types are concealed, V-VI types are residual (eluvio-deluvial) dispersion aureoles.

Of the most importance for prospecting are outcropping residual dispersion aureoles from mineral deposits (type I) that have permitted the large-scale effective use of conventional (terrestrial) lithochemical surveys in bearing-ore regions. These aureoles are due to deposits of any genetic types to be found in the upper structural stage in all regions subject to intensive denudation. In such environments only products of the weathering of the eluvio-deluvial type are formed at the surface of the country rocks. It is the mechanical dispersion that is principally responsible for the origination of residual dispersion aureoles. The most favourable conditions of their formation exist in mountainous areas which is shown by an inclination of the ground surface with type I aureoles (see Fig. 28) which does not rule out their formation in eluvial landscapes in erosion peneplains and flat watersheds. The most essential results of geochemical exploration—the discovered new economically important deposits of nonferrous, rare metals and gold both in this country and elsewhere are largely due to the secondary lithochemical dispersion aureoles of this particular type. In the general case the shape of a secondary residual dispersion aureole is a larger-size replica of the contour of a mineralization exposed at the surface of bedrocks. Under conditions of a rugged topography outcropping residual aureoles may be formed by horizontal beds of deposits of a residual genesis or ancient-origin weathering crust (see Fig. 28, Type Ia), although this type of aureoles are particularly important for prospecting for steeply inclined endogenic and sedimentary metamorphogenic deposits (Fig. 28, Type Ib). This is also true of such conditions where only the primary halos of orebodies have been attacked by weather-
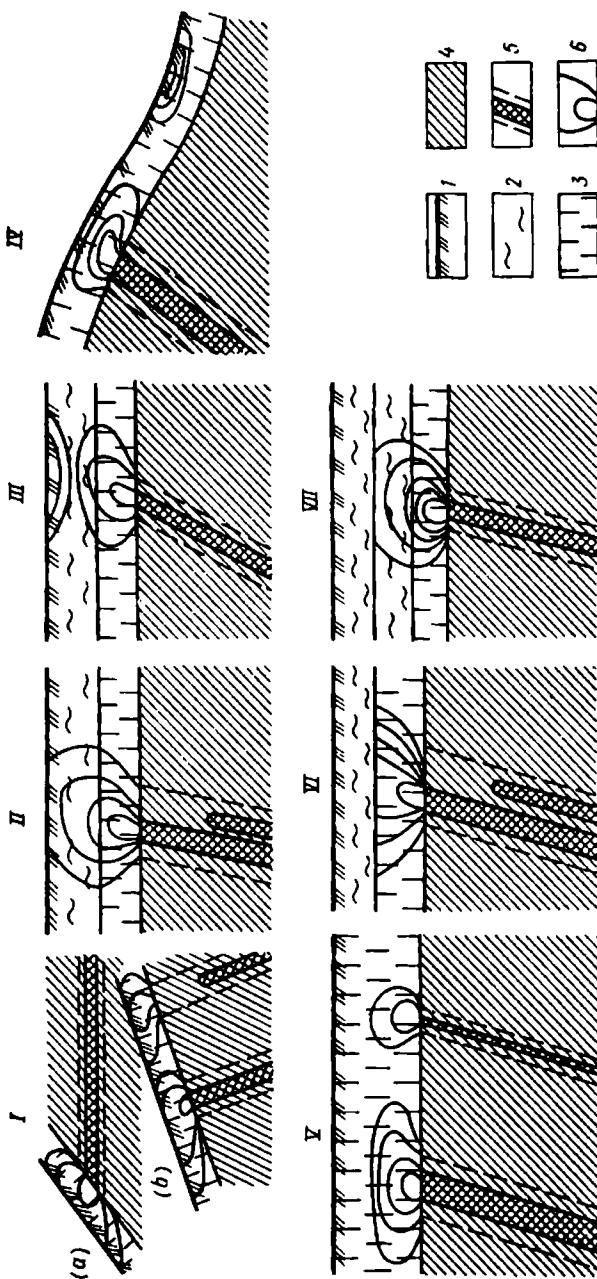
FIG. 28. Principal types of secondary lithochemical dispersion aureoles of ore deposits:

1—residual eluvio-deluvium (*a* and *b*); II—diffusional; III—supraore; IV—detached; V—leached and extremely impoverished; VI—concealed; VII—superimposed concealed. *1*—soil and vegetation cover; *2*—allochthonous sediments; *3*—modern eluvio-deluvium or ancient weathering crust of enclosing rocks; *4*—enclosing rocks; *5*—orebodies and their primary halos; *6*—secondary dispersion aureoles

ing and denudation. For example, a copperpyrite ore deposit was discovered in the South Urals in 1958 by sinking boreholes into the secondary residual aureole of Cu, Pb, Ag, Ni, Co located by a terrestrial lithochemical survey which was formed due to a primary halo of a blind orebody. Secondary residual Pb dispersion aureoles had been discovered before they were revealed by the drilling operations above the No. 23 North and No. 29 South deposit blind occurrences of the Achisai polymetallic deposit, respectively, at depths 240-350 m and 25-70 m.

Outcropping superimposed diffusional aureoles (Type II) are characteristic for lowlands with a blanket of allochthonous (i.e. transported other than *in situ*) sediments of minor thickness, principally in moderately humid and arid regions (see Fig. 28). These aureoles are predominantly due to the dispersion of soluble ore components; sometimes superimposed mechanical dispersion aureoles of stable ore minerals could be observed. The shape of a superimposed diffusional aureole and that of a primary orebody may be related in a number of ways. Owing to the varying thickness of allochthonous sediments, such type of aureoles may pass along the strike to buried types (VI and VII), alternate with intervals of an outcropping residual aureole (Type I) or be substituted by superimposed supraore aureoles (Type III). The range of diffusion is in theory unlimited. If the duration of geological time periods is to be taken into account, there is no limiting value for the thickness of allochthonous sediments through which the superimposed aureole of a deposit may in principle penetrate. In practical terms this limiting value is determined by a rapid decrease of the contrast index of a geochemical anomaly, i.e. the value of the signal-to-noise ratio found from Eq. (10). Other factors being equal, the depth of penetration of lithochemical exploration may be enhanced by resorting to more sophisticated methods of exploration, as has been pointed out when discussing the concept of "concealed" aureoles.

Supraore (Type III) and detached (Type IV) superimposed aureoles form under conditions where salt dispersion is occurring jointly with an opposite process of the migration of ore elements, i.e. their supergene accumulation. The common feature suggesting their accumulative origin is mirrored in the name of these two aureole types. Outcropping superimposed accumulative supraore aureoles (Type III) differ from superimposed diffusional ones by the presence of deep-seated allochthonous sediments where the available techniques fail to reveal aureoles in a vertical direction. On the one hand, supraore aureoles are hard to distinguish from landscape geochemical anomalies that occur at various geochemical barriers as a result of a supergene accumulation of metals from the immediate environment and are not associated with a primary mineralization at the depth. Such geochemical anomalies, vanishing with depth, were generally

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considered as barren, yet it may be assumed that some of them, believed to be useless in prospecting, may have been associated with an economically important mineralization. In view of the utmost importance of pinpointing buried deposits in covered ore regions the mechanisms of the formation and methods of discovery of super-imposed dispersion halos of Types II-III are discussed in detail in Sec. 3.8.

Detached accumulative (Type IV) aureoles resemble supraore ones described above differing in the absence of a cover of allochthonous sediments and a distinct shift from the orebodies toward the trend of modern runoff. Under such conditions ore deposits will form out-cropping (Type I) dispersion aureoles. It is only ore elements that in a particular geochemical landscape environment exhibit high liability to aqueous migration that may form concealed aureoles leached at the surface (Type V). The following accumulation of ore elements with a contrast migrational capacity in the supergene zone (see Sec. 1.8) in an altered geochemical environment gives rise to secondary detached hydromorphic aureoles superimposed on the local eluvio-deluvium and alluvial-proluvial sediments. In the latter case these aureoles may directly change into a lithochemical dis-persion flow. Detached Mo and U aureoles have been, e.g. observed in mountainous taiga areas of the Transbaikal Region. In oxidation conditions of amply wetted and moderately eroded slopes of a humid zone these elements form solutions and are leached out of the upper horizons of residual dispersion aureoles. As rain water runs to swamped valleys, very mobile, hexavalent Mo and U are deposited at a re-ductional barrier in a tetravalent form. Similar accumulations of ore elements (e.g. Cu) occur when passing from the low pH values in a zone of sulphuric decomposition to a neutral or weakly alkaline environment. Detached salt lithochemical aureoles may have resulted from the upward movement of subsurface mineralized waters washing a blind deep-seated orebody.

Type V-VII secondary lithochemical dispersion aureoles are classed as "concealed" ones. Leached and extremely impoverished aureoles (Type V) originate in eluvio-deluvium and are classed as residual. They are similar in their characteristics but differ in terms of agen-cies that have rendered them concealed. As has been already pointed out, residual aureoles leached at the surface are typically formed by elements manifesting intense aqueous migration in humid areas under conditions of retarded denudation. The leached layers of the modern eluvio-deluvium cover of the USSR territory are seldom more than 0.5-0.8 m in thickness. Sometimes one may observe accu-mulations of very mobile elements in the B-horizon known also as the illuvial horizon. Ore elements may be removed in humid tropical landscapes and ancient-origin weathering crusts, for example, from a white kaolinite horizon which may be 10 m and more thick. It

appears, however, that even extremely mobile chemical elements, such as F, Mo and U are not so often leached completely from residual dispersion aureoles. According to the findings of E. N. Vasilyev, outcropping residual phosphorus dispersion aureoles are preserved in a vertical section of the weathering crust of appreciable thickness under conditions of smooth relief and humid environment in the southwestern regions of equatorial Africa.

Extremely impoverished concealed aureoles form as a result of a naturally occurring dispersion directed toward the most complete equalization of element concentrations. If the initial metal content in a vertical section of the ore zone M_p, m%, was relatively small, maximum metal content values in the upper horizons of the dispersion aureole may not differ from the general local background variations. Since the intensity of a supergene dispersion diminishes with depth, the residual aureole of such mineralization is revealed only at some depth from the ground surface and should thus be considered as a concealed one. Concealed aureoles of this type are called "weakened at the surface". Concealed secondary aureoles in the modern eluvio-deluvium are especially typical for minor-scale mineralizations, in particular, for primary halos of blind orebodies. A rich and large orebody will give rise to an outcropping residual aureole under identical geological conditions.

Buried residual dispersion aureoles (Type VI) are analogs of

FIG. 29. Concealed residual dispersion pattern (North Kazakhstan). After A.N. Eremeev and A.P. Solovov:

1 — Neogene Quaternary loams; 2 — Triassic-Jurassic weathering crust; 3 — enclosing granitoids; 4 — fracture zone; 5 — ore element isoconcentration lines in conventional units; 6 — boreholes of exploratory by using a vibro-penetrator; 7 — core drilling boreholes; 8 — representative horizon for sampling

modern eluvio-deluvium aureoles. They differ from the latter in that they form in paleogeographic environments and are then overlain by sediments of more recent origin. Aureoles of this type characteristically occur in regions that for a lengthy time interval were found in continental conditions at a period preceding the accumulation of recent sediments and the peneplain surface of which preserved the ancient residuum. Viewed in a vertical section of the weathering crust, buried aureoles are mushroom-shaped, often of an asymmetrical form determined by the dip and strike of the orebody and direction

of the paleocurrent. They show a maximum coverage at the level of the multicoloured weathering crust which, in the particular case, provides a representative horizon for lithochemical exploration. In crushed rock weathering crust horizons the buried residual dispersion aureoles gradually diminish in area adjoining at deeper horizons orebodies and their primary halo. Aureoles of this type are not revealed in allochthonous deposits overlying the weathering crust. Figure 29 represents an example of a buried residual aureole actually discovered in a Triassic-Jurassic weathering crust overlain by Neogene-Quaternary loams. Buried residual aureoles of ore deposits found in weathering crusts of ancient origin are what gave rise to the elaboration of deep lithochemical methods permitting exploration efforts to be directed toward greater depths covered if lowland regions are involved.

Buried superimposed dispersion aureoles (Type VII) are, in turn, paleogeographical analogs of modern outcropping superimposed ones (Type II) overlain by sediments of more recent origin. The accumulation of ore elements in definite lithological superficial horizons owing to their water-bearing properties, bituminosity, carbonation and other features may lead to superimposed lithochemical aureoles which are buried counterparts of supraore or detached aureoles of Types III and IV. All that has been said about outcropping superimposed aureoles may be true as well for buried superimposed aureoles. If we deal with a covered mineralized region, their presence cannot be determined for sure for the entire area being explored.

Principal types (I-VII) of secondary lithochemical aureoles (see Fig. 28) are only generalized representations, departures from which will inevitably occur in the actual geological environment.

Sec. 3.3. A Mechanical Dispersion Aureole

The solid phase plays a predominant role in the formation of secondary residual dispersion aureoles from ore deposits. At the same time as disintegration of an orebody and country rocks enclosing its primary halo occurs, fragments that form in the weathering zone may move from the site of their original occurrence. This mobility of rock particles in the weathering zone is threefold: (1) the entire mass of particles may shift due to gravity as plastic deformations of the loose regolith or as local ruptures in the continuous cover; (2) separate rock particles may be removed from the surface of the regolith and then redeposited, e.g. moved in the direction of lower relief forms toward the base level of denudation and sedimentation zone; (3) particles proper may shift with respect to one another in the loose regolith. The roles played by the three types of mobility of particles in the formation of a dispersion field are essentially different. Moreover, in accordance with the law of inde-

pendence of the movements, each type of mobility yields a perfectly definite result.

Unless particles are redistributed relative to one another, the movement of the entire mass of particles cannot, as such, cause a mechanical dispersion aureole to be formed. What will be achieved is a shift and deformation of the dispersion aureole to be discussed later. The removal of particles and transport to the base level of denudation are responsible for the formation of a lithochemical dispersion flow and one rate or another of incessant rejuvenation of the dispersion aureole. If the particles are selectively removed, this process will cause the impoverishment or enrichment of the dispersion aureole. A mechanical dispersion aureole results from mutually shifting particles within the loose regolith formed by weathering products. The driving forces of this process are the agents of physical weathering: expansion and contraction of rocks due to temperature variations, freezing and melting of water, crystallization of salts, impact of meteoric water and wind action, effect of plant root systems and earth digging

FIG. 30. Diagram illustrating supergene mobility of particles:

1 — eluvium; 2 — bedrock; 3 — random particle mobility at different horizons

animals and invertebrates etc. The movement of an individual rock particle is small in amplitude, of random character, resembling, as it were, Brownian movement or thermal molecular movement. The root-mean-square of the range of flight of a loose rock particle during displacement may be approximated by a coefficient of mechanical dispersion σ. Particles are particularly mobile when located close to the ground surface and subjected to abrupt changes in temperature and water content, abundance of organisms inhabiting these horizons, decreased particle size etc. The absolute number of such shifts of an individual particle is in direct proportion to the time T_z elapsed since the moment it detached itself from the solid rock and, consequently, will be maximum at the ground surface and minimum at deeper horizons. Figure 30 is a schematic illustration of this regularity.

This mobility of rock particles is important for the formation of the dispersion field provided there is a local gradient of chemical element concentrations. All particles located at a limited area of the loose regolith formed by the disintegration of one rock species are, on the average, of the same chemical composition. Under such con-

ditions the movement of rock particles will cause no change in chemical element concentrations, since a displaced particle will be substituted by another one of identical composition. At the boundary of two different rock species and, particularly, at the contact of the country rock and the orebody the motion of particles may result in the appearance of a particle of a different mineral in place of one that has been transported. The geochemical mobility of elements (rate of mechanical dispersion) toward x, which is of interest to us, will be directly related to the concentration gradient $\frac{\partial C_x}{\partial x}$ in this direction. Mutual mobility of particles composing the loose regolith naturally causes movement of particles from sites of higher concentration toward areas of lower concentration thus forming mechanical dispersion aureoles.

Apart from the naturally occurring Au, Pt, cassiterite and chromite, quite a number of primary and secondary weathering-resistant ore minerals are subject to mechanical dispersion. These include scheelite, wolframite (tungstenite), beryl, chrysocolla, malachite, azurite, galena, cerussite, massicot, plattnerite and other lead minerals, smithsonite and calamine, baryte and witherite, cinnabar, apatite, zircon and baddeleyite, rutile, ilmenite, monazite, columbite and tantalite, pyrolusite, brownite, a number of secondary minerals of Ag, Ni, Co, Mo, Bi, Sb and many others. These minerals accumulate to form economically important deposits of primary ores or compose orebodies as outcrops in the weathering zone. These mineral forms of ore elements give rise to solid-phase residual lithochemical dispersion aureoles. The above transport of rock particles in the weathering zone may, under definite conditions, be sufficient to form secondary mechanical dispersion halos superimposed on the overburden sediments and manifesting features of diffusional origin (see Fig. 28, Type II). This may result, say, from cryogenic agitation of loose sediments that may penetrate to a depth of 3-4 m. In warm regions the action of various earth-boring animal species and invertebrates inhabiting the upper surficial horizons may be felt to a depth of 8-10 m. Taking into account the span of time life has been in existence on earth, it is responsible for the biological component of the mechanical dispersion of elements. Undoubtedly, it is possible for secondary superimposed halos to form in a solid state, but the mechanical migration of ore minerals is of principal significance for the origination of residual aureoles.

Sec. 3.4. Salt Dispersion Aureole

A secondary salt aureole forms if two principal conditions are satisfied: (1) ore elements are present as mineralized water soluble minerals; (2) the environment where dispersion occurs is water-

saturated. These two conditions are always met in the supergene zone. Loose products of weathering are liable to contain water. Even permafrost soils are no exception in this respect. According to the findings of E.M. Sergeev, capillary moisture in dispersed rocks of the weathering zone, given the capillary diameter is 0.24 mm, freezes at —13.6 °C; given a capillary diameter is 0.06 mm, at —18.5 °C, whereas the average temperature of permafrost soils in the south eastern regions of the Soviet Union is about 5-6 °C below zero. Even the driest soils to be found in arid areas do have moisture entrapped in them and may replenish their moisture content by condensating water vapours from the atmosphere. The behaviour of soluble salts in the dispersion field is governed by involved mechanisms of exchange chemical and physicochemical reactions, diffusion and capillary rise of solutions from deeper horizons toward the upper surface and is combined with evaporational and biogenic accumulation and removal of salts by meteoric water. Owing to the immense scope of geological time, even hardly soluble minerals are involved in the formation of a salt aureole. Hydromorphic halos, generally salt aureoles, are associated with the appearance of mineralized solution at the interface of the ground water table and the orebody through direct dissolution of the primary minerals of the lode or during their supergene alteration before they transform into stable secondary minerals. Of most interest for lithochemical prospecting is the formation of the salt aureoles of Cu, Pb, Zn, Au, Ag, As, Bi, Sb, Mo, Sn, Ni, Co etc. oxidizing sulphide deposits.

According to S.S. Smirnov, the development of a sulphide deposit oxidation zone is conditioned by the following general principles. The groundwaters located above the uppermost aquiclude freely interact with the ground surface. The percolation of meteoric water and water vapour condensation cause the ground waters to be incessantly replenished whereas the outflow to the surface drainage channels jointly with evaporation provide ground water discharge. The resultant hydrodynamic equilibrium between the water supply and discharge sets up an average phreatic surface which roughly agrees with the surface relief features (Fig. 31). The groundwater table (known also as the phreatic surface) is liable to seasonal and secular variations conditioned by the amount of precipitation. As the ground surface is being degraded due to denudation and hypsometric heights of discharge points are decreasing, the groundwater table is gradually sinking.

Meteoric water is saturated by oxygen and carbonic acid and shows oxidation capacity, the pH of common rain water being 6.0 (technogenic acidic rains are not discussed here). Its interaction with rocks produces a neutral or weakly alkaline reaction (the pH is 7.0-7.5). Due to pellicular and capillary water the seepage zone abounds in atmospheric gases which is responsible for oxidation con-

ditions prevailing in this zone. Below the water table there is less free exchange with the atmosphere. The low oxygen content and hydrolysis of minerals of rocks in the stagnant groundwater zone give rise to the alkaline reaction of the medium (pH > 7) where reductional environment dominates.

The principal sulphide minerals and their analogs exhibit negligible direct solvability which is in the range of 10^{-3}-10^{-22} g/l, but
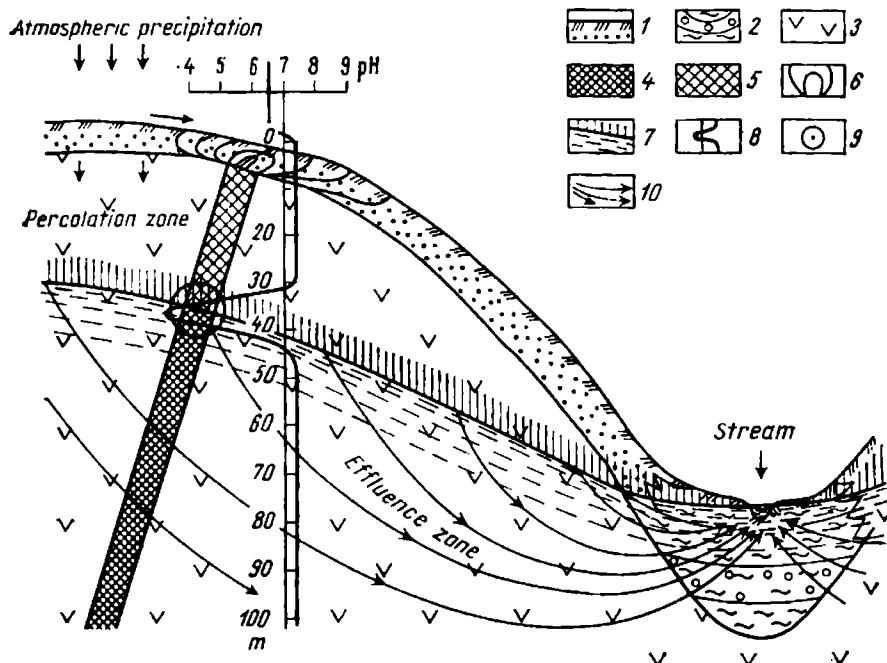

FIG. 31. Oxidation zone of sulphide deposit:

1 — eluvio-deluvium; 2 — alluvium; 3 — enclosing rocks; 4 — sulphide ores; 5 — oxidized ores; 6 — secondary residual dispersion aureole; 7 — ground water and capillary fringe; 8 — graph of variation of pH with depth; 9 — region of active occurrence of oxidation processes; 10 — direction of subsurface runoff

are unstable under supergene conditions and are readily oxidized in the seepage zone aqueous aerated conditions. The oxidation of pyrite, the most common sulphide, involves this reaction:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$
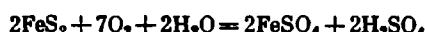
In the presence of free oxygen ferrous protoxide sulphate is unstable and changes to oxide sulphate:

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$$
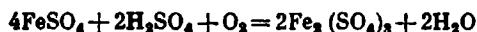
In diluted acidic waters $Fe_2(SO_4)_3$ is hydrolysed to liberate sulphuric acid:

$$Fe_2(SO_4)_3 + 6H_2O = \underline{2Fe(OH)_3} + 3H_2SO_4$$
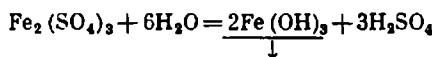
Precipitating from the solution, ferrous hydroxide eventually transforms into stable limonite $F_2O_3 \times nH_2O$. Free sulphuric acid is also produced by oxidation of many other sulphides. The presence of sulphuric acid is responsible for acid environment and an abrupt drop of the pH at the groundwater table close to an orebody. So, e.g. the SO_4^{-2} anion content in the oxidation zone waters of the Blyava copperpyrite deposit attained 123 g/l, the pH dropping to 1.0-2.0. The pH of waters sampled from exploratory bore holes sunk into the Gai copperpyrite deposit was 3.2-4.0, and that sampled from the "Vitriol Lake" linked with the deposit was 1.1, the SO_4^{-2} content being 2.6 g/l [15]. Such low pH values, however, as has been shown by numerous observations, most commonly are preserved only in the immediate vicinity to an orebody, without generally going outside its contours. The interaction with the country rocks usually brings about neutralization of acidic waters to form Ca, K, Na, Mg, Al sulphates. The pH rapidly increases in the immediate proximity to the orebody, and strongly acidic waters rather rarely occur along the periphery of a sulphide ore deposit. The intensity of neutralization of the acidic waters of the oxidation is particularly pronounced in carbonate rock.

The effect of sulphuric acid resulting from pyrite oxidation is to enhance dissolution and oxidation of massive sulphide ores. A particularly strong oxidizing and dissolving action is produced by ferrous oxide sulphate $Fe_2(SO_4)_3$. The potential difference of electrical polarization of various sulphides is a powerful oxidizing agent of multimineral ores [20]. Heavy metal sulphates, excepting anglesite $PbSO_4$ resulting from oxidation show high solubilities (Table 12) and may produce salt aureoles. However, with the pH increasing, these compounds are unstable, and relatively full removal from the oxidation zone is typical only for sulphur. What is of essential importance is the general direction of successive chemical transformations of the sulphide minerals in the oxidation zone: sulphide $\rightarrow$ sulphate $\rightarrow$ $\rightarrow$ carbonate $\rightleftarrows$ oxide (hydrosilicate, phosphate etc.). In this series of transformations the process is oriented toward substitution of readily solvable unstable sulphates by dissolution resisting stable minerals, end products of oxidation.

Oxidized sulphide ores on the surface of bedrocks form mechanical dispersion aureoles in the eluvio-deluvial formations in the course of weathering and denudation. This process is followed to one degree or another by the formation of salt aureoles. The area where mineralized solutions in an oxidizing sulphide deposit ori-

TABLE 12

The Solubility of Main Minerals in Water in the Zone of Sulphide Oxidation of Deposits

Mineral	Composition	Solubility, mole/l	Solubility product
A. Readily soluble sulphates — intermediate (unstable) compounds			
Goslarite	$ZnSO_4 \cdot 7H_2O$	531.2*	—
Morenosite	$NiSO_4 \cdot 7H_2O$	274.8*	—
Bieberite	$CoSO_4 \cdot 7H_2O$	265.8*	—
Melanterite	$FeSO_4 \cdot 7H_2O$	263.0*	—
Chalcanthite	$CuSO_4 \cdot 5H_2O$	172.0*	—
B. Hardly soluble, end products of oxidation			
Anglesite	$PbSO_4$	$1.35 \cdot 10^{-5}$	$2 \cdot 10^{-8}$
Barite	$BaSO_4$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-10}$
Cerussite	$PbCO_3$	$3.9 \cdot 10^{-7}$	$3.6 \cdot 10^{-14}$
Smithsonite	$ZnCO_3$	$1.7 \cdot 10^{-4}$	$2.7 \cdot 10^{-8}$
Witherite	$BaCO_3$	$9 \cdot 10^{-5}$	$8.1 \cdot 10^{-9}$
Spherocobaltite	$CoCO_3$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-12}$
Cerargyrite	$AgCl$	$1.25 \cdot 10^{-5}$	$1.8 \cdot 10^{-10}$
Malachite	$2CuO \cdot CO_2 \cdot H_2O$	—	$6 \cdot 10^{-34}$
Azurite	$3CuO \cdot 2CO_2 \cdot H_2O$	—	$1.3 \cdot 10^{-45}$
Powellite	$CaMoO_4$	$5.6 \cdot 10^{-5}$	$3.2 \cdot 10^{-9}$
Wulfenite	$PbMoO_4$	$3 \cdot 10^{-6}$	$8.5 \cdot 10^{-16}$

Note. The solubility, denoted by *, is given in g/l.

ginate constantly is the orebody interval close to the water table. It is from this site that soluble compounds migrate as a result of the capillary rise of solutions to the ground surface, diffusion-induced transport of salts and slow removal of solutions in the direction of the ground water discharge. The effluence of mineralized waters contributes to hydro-and lithochemical dispersion flows.

Diffusion of solvable salts stable at low pH values causes migration toward the ground surface and in lateral directions where the pH rapidly increases. In the changed geochemical conditions metals precipitate as dissolution-resistant hydroxides on the periphery of the salt halo.

In a diluted alkali environment Ag and Hg are preserved in the solution. However, in the presence of very common chlorine ion these metals do precipitate: Ag as cerargyrite (AgCl), and Hg as calomel (HgCl) and different oxychloride. Natural mercury specifically occurs in the oxidation zones of Hg deposits [9]. Over a vast range of pH values Mo is stable in solution soluble compounds of which, immediately following their appearance, give rise to insoluble ferrimolybdate, or molybdite ($Fe_2O_3 \times 3MoO_3 \times 7.5H_2O$).

Another cause responsible for bonding of water-solvable consti-
tuents of a salt aureole is the sorption of heavy metal cations by
various colloids in the supergene zone. Psilomelane ($MnO_2 \times nH_2O$)
exhibiting a pronounced adsorption capacity with respect to Cu,
Zn, Pb, Ni, Co and many other cations is a mineral commonly found
in the oxidation zone of sulphide deposits. In so doing, tetravalent
manganese precipitates already from acidic solutions. Clays, pri-
marily of montmorillonite compositions, characteristic for loose
materials in the weathering zone provide active sorbents of heavy
metals. There are clays that contain as chemical compounds and
products of sorption up to 20% of Zn, as much as several per cent
of Pb, more than 1% of Cu etc. A.A. Saukov [31] points out that
kaoline almost totally extracts copper from diluted solutions.
Adsorption-bonded, salt constituents acquire properties of solid
particles of loose rocks of the weathering zone and, as such, also obey
mechanisms of mechanical dispersion.

Whenever there is pellicular water in the environment, active
diffusion of salts in rocks occurs. Such conditions obtain even if
periodically in the percolation zone after rain fall or snowmelt.
Exchange chemical reactions, hydration and sorption cause "fixation
of the salt aureole" [29] by imparting to it properties of a stable
geological formation little dependent on sporadic precipitation.
Apart from that parameters of salt aureoles are governed by the
extent of aridity or humidity, i.e. the ratio between annual pre-
cipitation and evaporating capacity. It is possible to determine
the relationship between a salt aureole and climate without referring
to the genetic type of secondary dispersion aureoles, bearing in
mind that contours of residual mechanical aureoles may appreciably
differ from salt aureoles represented in Fig. 32.

If annual precipitation very much exceeds evaporability, the upper
horizon of soils are intensively washed out by meteoric water (pH
being 5-6), so, as a result, under conditions of retarded denudation
acid environment ($pH < 7$) is likely to occur corresponding to
a siallitic stage of weathering. The pH may amount to 4.5 in a water-
bogged area due to the organic acid content in the water. Excess
wetting facilitates the formation of concealed salt aureoles some
distance from the ground surface, leached residual or buried super-
imposed ones. An outcropping salt aureole is not ruled out, in partic-
ular, owing to biogenic or sorptional concentration of ore elements
in the uppermost soil layers. The occurrence of an outcropping salt
aureole in such climatic conditions is generally facilitated by a low
depth of the water table. These geochemical conditions are typical
for northern regions of the European Soviet Union and are mani-
fested in soil and geological terms by commonly occurring podzol
and grey wood soils. Arid regions showing pronounced evaporability
compared with precipitation provide a totally different conditions

for the formation of salt aureoles. Diffusion-induced migration of salts from the horizon where mineralized solutions originate may be augmented by accumulation of salts in the topsoil horizons following the familiar mechanism of soil salinization. Owing to inappreciable precipitation the mineral content of ground and soil water in the vicinity of an orebody and its salt aureole may attain very large
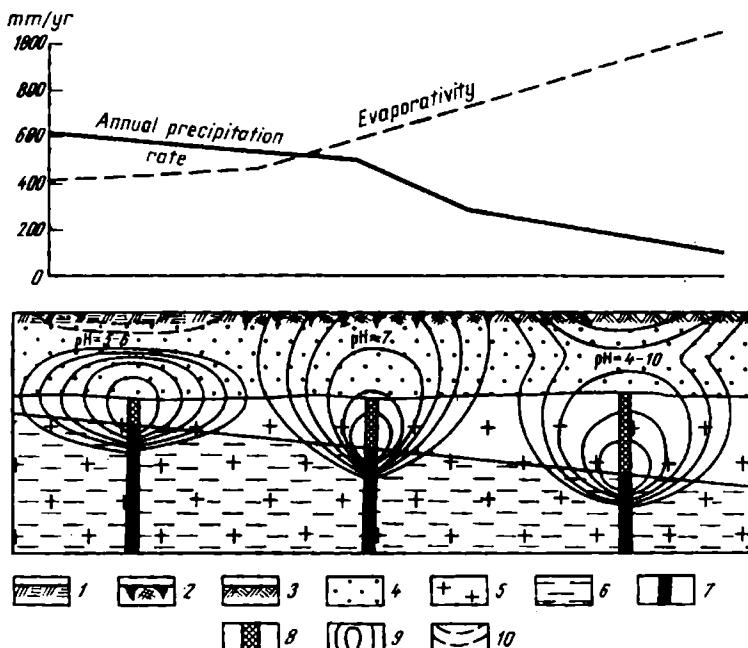

FIG 32. Interrelation between salt dispersion aureole and climate:
1 — Podzols and gray forest soils; *2* — Chernozem soils; *3* — brown soils, southern Serozem, Solonets and Solochak soils; *4* — looze sediments; *5* — bedrock; *6* — groundwater; *7* — primary sulphide ores; *8* — oxidized ores; *9* — isoconcentration contour lines; *10* — possible isoconcentration contour lines

values, and the pH values may vary over a vast range governed by ore mineralogy and local conditions. So, in arid regions of deserts of the Soviet Middle Asia, the pH < 1 values have been recorded in a sulphur deposit oxidation zone due to the presence of free sulphuric acid in loose sediments. Maximum pH = 10 was observed under similar environmental conditions in alkali soils of Sudan [23]. The salt aureoles in temperate zone areas are intermediate.

Sec. 3.5. Residual Dispersion Equation

It is the well-known principles of diffusion that are conveniently used to provide characteristics of salt dispersion in homogeneous rocks in physicomathematical terms. Whether these principles are

applicable to the mechanical dispersion of solid products of weathering which plays a dominant role in residual lithochemical aureoles is less evident and calls for further substantiation.

It may appear that the discrete nature of the dispersion field—the plurality of types of composition and size of rock and ore fragments, non-uniform saturation of the solid phase by water, air, vegetation, animal organisms or their remnants—makes its rigorous analysis difficult or even impossible. Things are different in reality and that it is feasible to work out a physicomathematical theory of a supergene dispersion field is evidenced by the successful application of laws of mechanics of continuous media to solutions of practical tasks although we know of the discrete filling of the space by atoms and molecules of solids, liquids or gases. That it is legitimate to treat a substance as a continuous medium follows from the infinitesimal size of molecules and interatomic distances compared with the man-size world, the immense numbers of these molecules contained even in a small volume of matter, infinitesimal time intervals between individual thermal motions of molecules compared with time intervals actually experienced by us. Detached from the molecular structure of matter, we regard a real liquid or gas as being a hypothetical continuous medium which made it possible, in particular, to create rigorous laws of hydro- and aerodynamics. Over a wide spectrum of geological conditions the properties of a continuous medium may be ascribed to loose materials in the dispersion field, whether they be of finely dispersed or clastic origin. A crucial role is being played here by the macrodimensions of the targets of investigation (geochemical field portion, aureole, flow) compared with minor-scale processes in the loose soil mass, by the infinitely large number of mineral particles or fragments involved in the process, and by the immense periods of geological time taken for a dispersion field to change any appreciably compared with short time intervals taken by our observations. In fact, the number of molecules N in 1 cm^3 of water is 3.3×10^{22}; in 1 cm^3 of a gas at an atmospheric pressure $N = 2.7 \times 10^{19}$. The minimum volume of a loose material to be considered may be taken to be 1 m^3. Given this volume, the number of clay particles, 1 μm in diameter, will probably be 1 $\times 10^{18}$, and for finer grain sizes will much exceed this quantity. Accordingly, for a portion of the ground surface 1 000 by 1 000 m in area, given that the thickness of the loose mass is 2 m, the number of 0.1 mm average grain size particles will be 2 $\times 10^{18}$; for 0.01 mm grain size, 2 $\times 10^{21}$. The number of 0.1 m diameter fragments in the same volume will be 2 $\times 10^9$, yet for larger diameter fragments this straightforward relationship becomes less evident.

In order to provide more substantiation for drawing analogies between the properties of a liquid (or gas) and those of rocks of the dispersion field we must recall *the principle of similarity* in mechanics

adequately elaborated for solutions of physical problems and, in particular, applied to modelling geotectonic processes. According to this principle, so that the similarity between events be observed as one of the constants of the target under study changes, all other constants of the target must be varied taking into *account the dimensionality* of the constants. Otherwise, a simple quantitative alteration of one of the parameters will give rise to a limit at which the substance will acquire new qualitative properties which provides a graphic illustration of transformation of quantity into quality.

Actual liquids have a coefficient of dynamical viscosity from 10^{-4} (ether) to 10^2 (castor oil at 20 °C), the viscosity of water at 20 °C is about 10^{-3} Pa $\times$ s. The behaviour of these fluids is observed at common time intervals of the order of 10^{-1} to 10^3 s. The duration of geological time periods is measured by quantities of a quite different order of magnitude and is 3×10^7 s (a year) to 3×10^{16} s (hundreds of millions of years) and more. The dimensionality of the coefficient of viscosity is $[\mu] = [ML^{-1}T^{-1}]$ and, consequently, will be displayed by bodies having the coefficient of viscosity multiplied by a respective factor, provided that other parameters of the medium are constant and active forces are only due to the change of the time scale. The change of the linear scale by a factor of 100 or 1 000 will extend these limits, since the principle of similarity in mechanics follows this relationship

$$\mu = \lambda\tau$$

where μ is the scale of viscosity change; λ is the scale of change of linear dimensions; τ is the scale of time change.

Thus, in the intervals of geological time, taking into account the dimensions of targets of search, the properties of actual liquids may be expected in solids manifesting a viscosity 10^6-10^{19} Pa $\times$ s and more. All that has been said above makes it possible to regard loose rocks in the dispersion field as being a continuous medium in which processes occur that are approximated by diffusion in a liquid phase whether solvable or solid constituents of aureole are involved. This makes it possible to extend a concept of supergene ore particles to fragments of any size and a colloidal dispersion fraction carrying ore elements in the state of sorption and to genuine solutions in which the ore elements appear as ions. Acted on by agents of weathering or molecular forces, all the particles are in continuous random motion the nature of which has been considered above (Sec. 3.3). The displacement of an individual particle of the regolith with respect to the plurality of the surrounding particles is classed as random events, i.e. ones that under given conditions and within a given time interval are as likely as not to occur. The random onset of mobility of a large number of particles within a large time period may have a definite frequency rate characterizing the probability of a statisti-

cal process. Under natural geological conditions the two require-
ments are satisfied. That is why an exactly regular distribution of
individual particles will be due to their random motions. This dis-
tribution in a dispersion field of ore particles is what is considered
by us as the secondary lithochemical aureole of an orebody. In math-
ematical terms the problem of a lithochemical dispersion aureole
may reduce to the determination of a distribution function of ore
particles depending on the active
forces, parameters of the me-
dium, space coordinates and time.

Let us consider the distribution
of ore mineral particles in
a plane across the strike of an
orebody and relatively far from
its extremities to rule out their
effect (Fig. 33). To simplify
matters, let us suppose that the
ground surface is horizontal and
parallel to *yox* plane, and let us
align the axis of the orebody in
the shape of a vertical thin vein
manifesting a constant linear
metal amount M with *oz* line.
At the initial time moment
$T = 0$ (before the onset of weath-
ering) all ore mineral particles
were concentrated along *yoz*
plane over an interval of a ne-
gligibly small thickness. Then
(due to weathering) the particles

FIG. 33. Concerning the derivation
of a dispersion equation:
1 — eluvio-deluvium; *2* — bedrock; *3* — ore-
body; *4* — location of orebody before
weathering

began to move making individual "jumps" of different length and
direction in *xoz* plane within a time interval $T > 0$. By virtue of
the adopted constant metal values in an orebody $(C_p = \text{const})$
and in the immediate surroundings $(C_0 = \text{const})$, and, consequently,
the existing initial conditions $\dfrac{\partial C}{\partial y} = \dfrac{\partial C}{\partial x} = 0$, given $T = 0$, the dis-
persion of ore material within an elementary layer Δz, in the first
approximation, may be considered as governed by x only. The ensuing
increase and decrease of ore particles at the expense of over- and
underlying horizons of aureole for such an elementary layer can be
regarded as balanced, and we can dispense with the boundary layer
at the ground surface as one that is constantly being rejuvenated by
denudation. Owing to the symmetry of the conditions, deflections
of the particles to the left or right of *oz* line seem to be equally prob-
able, and the formation of a lithochemical aureole must be con-
sidered as a process of lateral dispersion (see Fig. 33).

Thus stated, the physical aspect of lithochemical dispersion makes it possible to compare it with a problem of distribution of temperatures in the environment, if at the initial time moment $T = 0$ in yoz plane some amount of heat is released, or with a similar problem of diffusion. Its solution reduces to the integration of a linear differential equation with parabolic type second order derivatives which is known as the Fourier equation which appears for the case of a one-dimensional (linear) dispersion as:

$$\frac{\partial C_x}{\partial T} - D\frac{\partial^2 C_x}{\partial x^2} = 0$$

where D is a coefficient of diffusion.

Its solution, determining an exponential relationship between C_x and x, can be found in mathematical physics courses. It is only to better determine geological relationships between the active forces, parameters of the medium, space coordinates and time that we present a graphical but not very rigorous derivation of a lithochemical dispersion equation the calculations based on which yield identical results. Given the previous conditions of the problem, let us determine the amount of the ore material dM displaced within a time interval ΔT across a unit area $\Delta y \Delta z$ at a randomly chosen point on the x axis (see Fig. 33) at a concentration gradient of ore material at this point $\frac{dC_x}{dx}$. Note that it is possible to determine the amount of the material in terms of the number of particles or weight, whichever is better. The amount of the material dM will be in direct proportion to the concentration gradient, size of the unit area, time of observation, and in reverse proportion to the coefficient of viscosity of the medium μ, or:

$$dM = -\varepsilon_1 \frac{1}{\mu}\frac{dC_x}{dx}\Delta y\,\Delta z\,\Delta T$$

where ε_1 is a proportionality coefficient.

Yet, on the other hand, at a point x at a particular moment of time only such particles can be found that move at some fictitious velocity x/T and that, within the time period T, have travelled from the original position in yoz plane to the location of the profile in question. Consequently, dM is proportional to the number of particles C_x (concentration) and their fictitious velocity, or

$$dM = \varepsilon_2 C_x \frac{x}{T}\Delta y\,\Delta z\,\Delta T$$

By equating these two relationships and making short cuts we get

$$C_x \frac{x}{T} = -\varepsilon\frac{1}{\mu}\frac{dC_x}{dx}$$

where $\varepsilon = \varepsilon_1/\varepsilon_2$; T is a local parameter characterizing the duration of the weathering process.

Owing to the smallness of the time taken by our observations of aureole compared with the geological time, the observed distribution of particles due to the dynamic equilibrium between the weathering and denudation is considered as being constant and the particles themselves as being stationary for the given moment. By dividing the variables and integrating this differential equation we have:

$$\ln C_x = -\frac{\mu}{2\varepsilon T} x^2 + \ln C$$

where $\ln C$ is a constant of integration.

By getting rid of logs and introducing a literal definition $\sigma^2 = \dfrac{\varepsilon T}{\mu}$ we obtain

$$C_x = C\, e^{\frac{-x^2}{2\sigma^2}}$$

The value of the constant of integration will be found from the value of concentration at the midpoint of the aureole. By virtue of the symmetry of the conditions at $x = 0$ we have $C = C_{max}$, or

$$C_x = C_{max}\, e^{\frac{-x^2}{2\sigma^2}} \tag{52}$$

Ore material particles in a dispersion field cannot randomly originate or disappear, rather, they are redistributed along the x axis, gradationally passing from a state of primary concentration in the orebody to that of secondary dispersion in the mass of the regolith. The total amount of ore in a dispersion aureole of an infinite area with a cross section equal to unity will remain constant and be equal to M, or

$$M = \int\limits_{-\infty}^{+\infty} C_x\, dx = C_{max} \int\limits_{-\infty}^{+\infty} e^{-\frac{x^2}{2\sigma^2}}\, dx$$

This relationship, known as the Poisson integral, is equal to $\sigma\sqrt{2\pi}$, or

$$M = C_{max}\sigma\sqrt{2\pi} \tag{53}$$

$$C_{max} = \frac{M}{\sigma\sqrt{2\pi}} \tag{54}$$

By inserting this value of C_{max} into Eq. (52) and taking into consideration that $C_0 \neq 0$, we finally get:

$$C_x = \frac{M}{\sigma\sqrt{2\pi}}\, e^{-\frac{x^2}{2\sigma^2}} + C_0 \tag{55}$$

Thus, the distribution of ore particles in a residual lithochemical dispersion aureole of a thin vertical vein minus the background value conforms to normal distribution with parameters M and σ being governed by the characteristics of the mineralization and local conditions. Given $C_0 = 0$, $M = 1$ and $\sigma = 1$, Equation (55) assumes this form:

$$C_x = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}}$$

which is known to be a normalized function of normal distribution. The values of this function $C_x = f(x)$ and the respective integral function

$$\Phi(x_i) = \frac{2}{\sqrt{2\pi}} \int_0^{x_i} e^{-\frac{x^2}{2}} dx$$

are tabulated in mathematical reference books. We have met with the normal distribution of element contents (or their logs) when considering metal background values in samples (see Sec. 1.3). In this particular case, however, these identical mathematical laws have nothing in common. Equation (55) characterizes the relationship between the metal content C_x at a given point and its distance x from the centre of aureole. This relationship establishes regularities governing particular metal contents at observation points unambiguously conditioned by the local parameters and coordinates. Referred to Eq. (3) characterizing the distribution of metal content background values, the quantity $x = C_i$ is an argument, and the function is represented by the frequency rate (n_i) at which one metal background value or another, larger or smaller than the average metal content C_0, randomly occurs. At this, one cannot tell in advance what particular metal content C_x is likely to be found at a point with specified coordinates. What one may do is only evaluate the probability that the metal content at any point will be within definite limiting values or exceed these latter. Unlike the statistic distribution of metal content background values, $n_i = f(C_i)$ which is approximated by a normal or lognormal distribution, relationships $C_x = f(x)$, Eq. (55) and similar equations follow from solutions of mathematical problems of active connections underlying the geological process. These theoretical functional relationships illustrate spatially ordered distributions of chemical elements in anomalies.

As follows from consideration of tabulated values of the normal distributions, the residual lithochemical aureole is characterized by a symmetrical rapidly diminishing function with one peak at the origin of coordinates which coincides with the epicenter of the lode provided that the ground surface is horizontal and the dip of

the orebody is vertical. The parameter σ in Eq. (55) has the meaning of a dispersion coefficient governing the particular type of graph of metal concentrations in aureole. As can be seen from Fig. 34, an increase in the dispersion coefficient σ, given a constant linear quantity of metal M in the orebody, causes the form of the secondary residual aureole to become even flatter which mirrors a gradual dispersion of the useful mineral particles in the mass of weathering products of the country rocks. Since the power index in the exponent $x^2/2\sigma^2$ is dimensionless quantity, we find that the dimensionality of $[\sigma] = [x] = L$. By expressing x in metres we conclude that the value of the dispersion coefficient is also expressed in metres characterizing a root-mean-square removal of ore particles during supergene dispersion from their primary sites in the orebody which is consistent with the physical nature of the linear dispersion we have considered. The physiogeological meaning of parameters of M stems from the fact that this is the total (linear) ore (metal) amount in aureole distributed along the x axis equal to its amount M_p in the same section of the orebody before the onset of weathering. In an idealized

FIG. 34. Graphs of secondary residual dispersion aureoles from an ore vein or different values of coefficient of dispersion σ:

1 — eluvio-deluvium; *2* — ore vein; *3* — enclosing rocks

residual aureole this will yield the following relationship:

$$M = M_p = C_p \times 2p \qquad (56)$$

where p is the semithickness of the primary mineralization that gave rise to the aureole.

If, as is usual, C_p is expressed in per cent and p in metres, the value of M will be measured in metre per cent (m %). In geometrical terms, given $C_0 = 0$ (i.e. minus the background values), the value of M characterizes the area bounded by the graph of aureole $C_x = =f(x)$ and the abscissa axis. Equation (56), valid for orebodies of any thickness, makes it possible to elucidate the concept of a "thin" orebody or seam, for which

$$C_p \times 2p = C_{max}\sigma \sqrt{2\pi} \qquad (57)$$

The random mobility of particles tends to equalize ore concentrations so the maximum metal content in the secondary residual dispersion aureole is unable to exceed the original metal content in the orebody, or $C_p \geqslant C_{max}$, whence

$$2p \leqslant \sigma \sqrt{2\pi} \approx 2.5\sigma \tag{58}$$

Consequently, orebodies whose semithickness is $p < 1.25\sigma$ may be considered as being "thin". Secondary dispersion aureoles of such bodies obey *the equivalence principle* of the thickness of a mineralization and its metal content, for the form of aureoles, by virtue of Eq. (56), is governed not by these parameters taken separately, but by their product. Consequently, there may be a multitude of various pairs of values of C_p and $2p$ that will yield the same value of parameter M m%, and identical residual aureoles at constant values of σ are formed owing to the occurrence of different "thin" orebodies.

By contrast, dispersion aureoles of orebodies of appreciable thickness ($p > 1.25\sigma$) no longer obey the normal distribution, Eq. (55), halo graphs display flat peaks, and Eq. (57) is violated.

R.I. Dubov [6] has proposed a mathematical substantiation of the formation of the residual aureole of an orebody of whatever thickness. Suppose an orebody of an infinite length extended along the y axis, $2p$ in thickness, with its centre at the origin of coordinates and a constant metal content C_p is sliced into thin seams $\Delta\xi$ in thickness, each containing an amount of metal $\Delta M = C_p \Delta\xi$ (Fig. 35). Then, according to Eq. (55), the dispersion component of each of these seams will be found from this relationship.

$$\Delta C_x = \frac{C_p \Delta\xi}{\sigma \sqrt{2\pi}} e^{-\frac{(\xi-x)^2}{2\sigma^2}}$$

where ξ is a distance from the origin of coordinates to the centre of a unit seam that may take on values from $-p$ to $+p$.

In conformity with the principle of superposition, the metal content at a point x governed by the total assemblage of thin seams
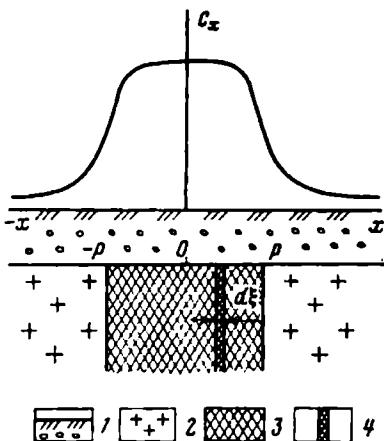
FIG. 35. Graph of a residual dispersion aureole $C_x = f(x)$ over a thick orebody:

1 — eluvium; *2* — enclosing rocks; *3* — orebody $2p$ in thickness; *4* — elementary ore seam $d\xi$ in thickness with centre at point ξ

making up the orebody will be found as a sum of their effects. Passing to a limiting value lim $\Delta\xi \to 0$, we have

$$C_x = \frac{C_p}{\sigma\sqrt{2\pi}} \int\limits_{-p}^{+p} e^{-\frac{(\xi - x)^2}{2\sigma^2}} \, d\xi$$

For a given observation point x is a parameter, ξ is variable of an integration constant. The obtained integral may be conveniently transformed by substituting $\dfrac{\xi - x}{\sigma} = \tau$ and $d\xi = \sigma \, d\tau$. By varying the limit of integration and factoring σ outside the integral sign, we get

$$C_x = \frac{C_p}{\sqrt{2\pi}} \int\limits_{-\frac{p+x}{\sigma}}^{+\frac{p-x}{\sigma}} e^{-\frac{\tau^2}{2}} \, d\tau =$$

$$= \frac{C_p}{2} \left(\frac{2}{\sqrt{2\pi}} \int\limits_{0}^{\frac{p-x}{\sigma}} e^{-\frac{\tau^2}{2}} \, d\tau + \frac{2}{\sqrt{2\pi}} \int\limits_{\sigma}^{\frac{p+x}{\sigma}} e^{-\frac{\tau^2}{2}} \, d\tau \right)$$

The parenthesized terms are probability integrals whose numerical values are to be found in mathematical handbooks. By using the conventional notation of probability integrals as functions of their upper limiting values, we present the ultimate form of the obtained relationship:

$$C_x = \frac{C_p}{2} \left[\Phi \left(\frac{p+x}{\sigma} \right) + \Phi \left(\frac{p-x}{\sigma} \right) \right] + C_0 \qquad (59)$$

Thus the graph of the metal content values in a residual aureole of an orebody of major thickness in a profile removed from its extremities is governed by three parameters: C_p, p and σ. A substitution of the value of $x = 0$ into Eq. (59) yields the maximum metal content at the midpoint of the aureole (minus the background value):

$$C_{max} = C_p \Phi \left(\frac{p}{\sigma} \right) \qquad (60)$$

As is shown by tabular values of $\Phi(x)$, in an idealized residual aureole the value of C_{max} differs very little from C_p even at $p/\sigma > > 2.0$. Having transferred the origin of coordinates at the boundary of the orebody and assuming $2p \to \infty$, by referring to Eq. (59), we will find an equation for a secondary aureole above the contact of two rock varieties with a high, C_p, and a low, C_0, metal content:

$$C_x = \frac{C_p}{2} \left[1 \pm \Phi \left(\frac{x}{\sigma} \right) \right] + C_0 \qquad (61)$$

The plus sign preceding the probability integral corresponds to a case where a rock with a high metal content C_p is located in the area of positive values of x (Fig. 36), the minus sign is related to transition to background values in this area.

Since the strike of any orebody is limited, the profile for observations may be located close to its extremities. In this case $\frac{\partial C_y}{\partial y} \neq 0$, and the metal content in aureole takes on the form of a two-dimensional relationship $C_x = f(x, y)$. There is a straightforward solution of this problem for rectangular orebodies whose sides are $2p_x$ (thickness) and $2p_y$ (length along the strike) and which manifest a constant ore metal content C_p. Having placed the origin of coordinates in the centre of the orebody and defined by ξ and η the coordinates of a randomly chosen point in the orebody before the onset of its weathering, analogous to the previous relationship, we can write:

FIG. 36. Graph of a dispersion aureole over a contact of rocks:

1 — eluvium; 2 — rocks with metal content C_0; 3 — rocks with metal content C_p

$$C_x = \frac{C_p}{2\pi\sigma^2} \int_{-p_x}^{+p_x} \int_{-p_y}^{+p_y} e^{-\frac{(\xi-x)^2+(\eta-y)^2}{2\sigma^2}} \, d\xi \, d\eta$$

By dividing the double integral into two singular ones and by carrying out proper substitution, we finally obtain

$$C_x = \frac{C_p}{4} \left[\Phi\left(\frac{p_x+x}{\sigma}\right) + \Phi\left(\frac{p_x-x}{\sigma}\right) \right] \left[\Phi\left(\frac{p_y+y}{\sigma}\right) + \Phi\left(\frac{p_y-y}{\sigma}\right) \right] + C_0 \tag{62}$$

Hence, given $x = y = 0$, we will find the maximum metal content at the central point of aureole (minus the background value)

$$C_{max} = C_p \Phi\left(\frac{p_x}{\sigma}\right) \Phi\left(\frac{p_y}{\sigma}\right) \tag{63}$$

Consequently, the metal content distribution in the residual aureole of a rectangular orebody is governed by four parameters, C_p, p_x, p_y and σ. If the profile of observations found across the strike of the orebody is at a distance $y > 2\sigma$ from its nearest extremity, Eq. (62) is replaced by a one-dimensional relationship, Eq. (59),

and for thin orebodies at $p_x < 1.25\sigma$, by a normal distribution, Eq. (55). Theoretical metal contents in dispersion aureoles above ore bodies manifesting an elliptical (in particular, circular) planimetric contour differ not more than by 10% from those in aureoles above equivalent orebodies of a rectangular (in particular, square) shape, these differences decreasing as orebodies diminish in size compared with the value of the local dispersion coefficient σ [6]. A more rigorous analysis of residual dispersion aureoles would formally call for a solution of a three-dimensional problem $C_x = f(x, y, z)$. This is because as early as the first moments of the formation of the aureole $(T > 0)$ the condition $\frac{\partial C_z}{\partial z} = 0$ is disturbed since the parameters T and, consequently, C_z as well, are governed by depth. However, calculations show that, provided $C_p = \text{const}$, $M_p = \text{const}$, and σ_x diminishes monotonically with depth, the distributions in question differ from the three-dimensional relationships by not more than 5%. In practical terms this permits us to restrict ourselves to one- and two-dimensional relationships.

Sec. 3.6. Parameters of a Secondary Dispersion Aureole

It follows from the physicomathematical principles of supergene dispersion that the metal contents at the periphery of aureole asymptotically approach the geochemical background and obey the relationship $C_x \to C_0$, given that $x \to \pm\infty$. Consequently, the actual dimensions of secondary dispersion aureoles do not allow of rigorous determination and, theoretically, are infinitely great. This is another proof of a purely conventional, technical meaning of such quantities that are practically known as "dimensions" of aureoles (cf. Sec. 1.5). Parameters that provide objective characteristics of a secondary aureole associated with the primary mineralization and the local geochemical environment are: the maximum metal content in the aureole C_{max}, supergene dispersion coefficient σ, the amount of metal in aureole in a profile M m% or plan, the coefficient of the residual productivity k and some other geochemical index characteristics. The numerical values of these parameters are more precise, the greater is the accuracy of observations.

The maximum metal content at the midpoint of a residual aureole, in conformity with Eqs. (54), (60) and (63), given that the parameters of the mineralization are constant, is governed by the magnitude of the local dispersion coefficient σ, i.e. by the capacity to migration or geochemical mobility of ore elements in conditions of supergene aureole formation. Dispersion should not be confused with the possible partial transport of the ore element from aureole which is mirrored by the coefficient of productivity $k < 1.0$ that enters into Eqs. (18) and (19).

As we derived the function of dispersion, Eq. (55), we adopted the letter σ to denote the value of

$$\sigma = \sqrt{\frac{\varepsilon T}{\mu}} \qquad (64)$$

where ε is unknown proportionality coefficient.

To elucidate its meaning, let us refer to the dimensional method, bearing it in mind that $[\sigma] = L$, $[T] = T$ and $[\mu] = mL^{-1}T^{-1}$. By substituting these values into Eq. (64) and solving it with respect to $[\varepsilon]$, we have:

$$[\varepsilon] = mLT^{-2}$$

Consequently, ε has a dimensionality of a force, or

$$\varepsilon = \xi F,$$

where F is a force; ξ is a dimensionless (numerical) coefficient.

The ultimate form of the relationship for a supergene dispersion coefficient will be thus:

$$\sigma = \xi \sqrt{\frac{FT}{\mu}} \qquad (65)$$

The magnitudes of F, T and μ are governed by the geochemical landscape and geochemical environment and characterized by the particular values within the boundary of a particular polymineral dispersion aureole. Individual properties of ore elements during supergene dispersion are mirrored by the numerical value of ξ. Clearly, the degree of mobility of ore particles is conditioned by their shape and size, density and surficial molecular properties, i.e., in the long run, their chemical and mineralogical composition, the role played by non-mineral forms of occurrence of the ore element etc. The values of ξ may vary appreciably for different metals and mineral species within the boundary of one dispersion aureole.

As we were deriving a relationship for lithochemical dispersion we were not constrained by any added assumptions as to the nature of ore particles, so dispersion of particles of whatever type will obey the normal distribution. Since values of ξ even in aureole from one ore element are different, so will dispersion coefficients for particles of different mineralogical composition vary. Thus, we may expect the secondary residual aureole of a lead-bearing occurrence to concurrently contain primary galena and various secondary lead minerals, such as anglesite, cerussite, massicot, plattnerite, pyromorphite, phosgenite, cesarolite, wulfenite and many others including nonmineral forms. Each of these lead-containing compounds may be distributed in aureole manifesting various dispersion coefficients σ_{PbS}, σ_{PbSO_4}, σ_{PbCO_3}, σ_{PbO}, σ_{PbO_2} etc. This, however, will not imply any departures from normal distribution, Eq. (55), of total

lead contents in aureole which, whatever the form of occurrence of the metal, are determined, e.g. by emission spectroscopy of lithochemical samples. According to Lyapunov's central-limit theorem, the sum of a large number n of commeasurable random variables distributed normally and exhibiting parameters M_i, σ_i, is also distributed normally with these parameters:

$$M = M_1 + M_2 + M_3 + \ldots + M_n \text{ and}$$
$$\sigma = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \ldots + \sigma_n^2}$$

This property of stability of the normal distribution accounts for its extensive use in nature.

The quantities F, μ and T, governing the value of σ, vary with depth which causes changes in the numerical values of the dispersion coefficient in a vertical profile of the regolith. In the general case the value of the coefficient of viscosity of rocks μ in the weathering zone is the least near the ground surface in their most unconsolidated state, and is the largest at the solid bedrock horizon at the early period of the weathering. The magnitude of the active force F seems to diminish with depth owing to rapid decline in the amplitude of temperature variations and effect of external dynamic factors under the cover of the overburden, lesser role of biogenic processes etc. The duration of exposure to weathering T is likewise decreasing with depth and at the contact with the bedrock $T = 0$. That T is dependent on the z-coordinate is unambiguously shown by Eq. (50) for the case of a dynamic equilibrium between weathering and denudation. If F and T decrease with depth, and μ, even if it increases with depth, in Eq. (65) is found in the denominator, then the dispersion coefficient σ from its maximum value at the surface, $\sigma_0 = \sigma_{max}$, should diminish in magnitude and at the horizon of the bed rocks attain a value of $\sigma_h = 0$. By taking into account these limiting values without any additional assumptions as to the character of the functional relationships between μ, F, T on the one hand, and z on the other hand, we may assume the dispersion coefficient is a linear function of z and obeys this relation:

$$\sigma_z = \sigma_0 \frac{h-z}{h} \qquad (66)$$

The numerous studies of vertical sections of residual aureoles provide ample proof of this statement. The numerical values of σ referred to graphs of detailed lithochemical surveys apparently similar to their theoretical shape for a thin orebody (Fig. 37) are found by a "method of three levels". As is shown by tabulated values of normal distribution [34], the distance between the abscissas of points with ordinates $C_x = 0.607 C_{max}$ (minus background) for a theoretical curve corresponds to 2σ. The distance between the

abscissas for ordinates $C_x = 0.325 C_{max}$ corresponds to 3σ, and that between the abscissas for $0.135\ C_{max}$ is 4σ. This permits three independent determinations of the values of σ from the width of aureole, given three values of C_x. If the three values of σ found from the graph agree accurate to ± 10 to $\pm 15\%$ (which is within the accuracy of spectroscopic analysis), we may assume that the observed data satisfactorily agree with the theoretical ones, Eq. (55). Should the observed values of σ regularly decrease with increasing the interval of the graph from which they have been established, i.e. there is a relation σ (referred to $0.607\ C_{max}$) $>$ σ (referred to $0.325\ C_{max}$) $>$ $>\sigma$ (referred to $0.135\ C_{max}$), this suggests an orebody of substantial thickness. Use must then be made of Dubov's dot charts to determine the values of σ.

Theoretical models of the formation of secondary residual dispersion aureole are based on assumptions as to constant parameters of a mineralization, M_p, C_p, $2p$ referred to the dip of the orebody. This permits us to deal with constant amounts of metal in each horizon, M_z, in an idealized residual aureole through the entire vertical section of the eluvio-deluvium in the interval $0 \leqslant z \leqslant h$. For conditions, such that $M_z = M_p = $ const and the dispersion coefficient σ_z decreases with depth, Fig. 38 represents a vertical section of such aureole in isolines. Calculations have been made for intervals spaced at $0.1\ h$ at $\sigma_0 = 1.0$ and $h = 1.5\ \sigma_0$ for a thin vertical orebody and the horizontal ground surface. In this simplest case the profile of the secondary residual aureole appears as a fan expanding toward the ground surface.

FIG. 37. Relating to calculation of coefficient of dispersion σ by "three-level" method

Provided the spacing between sample points Δx along a traverse is uniform, the value of the parameter M is found from Eq. (15). If the spacing is non-uniform which may be often due to crowded sample points at the central part of the aureole, Eq. (15) is replaced by a more universal relationship

$$M = \sum_{i=1}^{n} \left(\frac{x_{i+1} - x_{i-1}}{2} \right) C_i - 2a C_0 \qquad (67)$$

where x_i is the abscissa of a point with the metal content C_i; $2a$ is the effective width of the aureole.

The origin for reckoning distances $x_0 = 0$ is provided by the first extreme point bounding aurole on the left-hand side of the profile where the metal content is $C_0 < C_A$. Given the value of σ for aureole with one distinct peak it is possible to calculate the amount of metal, M m%, by using Eq. (57), according to which

$$M = (C_{max} - C_0)\, 2.5\sigma \quad (68)$$

This relationship, however, yields only an approximate value of M, for the result obtained is entirely governed by the accuracy of the spectroscopic analysis at which the value of C_{max} has been determined. Equations (15) or (67) are best for practical purposes.

Equation (56) which establishes *identical amounts of metal* in idealized residual dispersion aureole M or in original primary mineralization M_p, is disturbed in a real geological environment, being replaced by a proportional relationship, Eq. (18). It is a matter of experience that the value of the coefficient of residual productivity $k \gtrless 1.0$ connecting the values of M and M_p may differ by a factor of many tens, being governed by the particular properties of the chemical

FIG. 38. Vertical cross section and graph of idealized residual dispersion aureole:

1 — eluvium; *2* — enclosing rocks; *3* — orebody; *4* — element isoconcentration contour lines in conventional units

elements, morphological features of the mineralization and local landscape conditions. Therefore it is necessary to know the numerical value of this parameter for the conditions that obtain in the region of interest to us and for principal ore elements. In the general case its value varies with depth, or $k_z = f(z)$, where $0 \leqslant z \leqslant h$, being governed by supergene processes of metal accumulation in particular horizons of the zone of weathering $(k > 1.0)$ or by its leaching from aureole $(k < 1.0)$. The leached metal may be moved to a dispersion flow and the end runoff reservoir, may be totally dispersed in the surrounding landscape or form secondary accumulations at the geochemical barriers within the contour of aureole or outside it. The accumulation of metal in a residual aureole compared with its initial amount in the primary mineralization may be linked, in particular, with gravitational mineral differentiation according

to density; with increased solubility of rock-forming minerals; with evaporational, biogenic or sorptional accumulation of ore elements at the ground surface. The local values of $k \geqslant 1.0$ in the profile of residual aureoles seem to be established within a relatively short period of geological time.

In case the removal of ore particles from the surface of a slope is delayed relative to that of ore-free particles, this will cause a relative accumulation of ore minerals in the upper horizons of aureole. As a result, the removal of ore particles will then be enhanced and the accumulation will be inhibited. These reciprocal processes will soon balance each other. The same self-regulating trait will be exhibited by the processes of selective solution of ore or rock-forming minerals. Simplified calculations show that a dynamic equilibrium is attained given $k = 2.0$, in less than 100 years under conditions when the duration of time taken for the upper horizon of a dispersion aureole to form is 10 thousand years (T_0).

General laws of the geochemistry of hypergenesis make it possible to determine *a priori* the values of coefficients of residual productivity k governed by landscape conditions of the formation of dispersion aureoles and by the properties of ore elements.

1. In mountainous regions undergoing active denudation, whatever geochemical landscape, owing to rapid rejuvenation of dispersion aureoles the individual differences between the chemical elements are levelled, and for all ore elements values of $k \approx 1.0$ may be expected.

2. In humid zone regions with mild relief and inhibited denudation for elements liable to active aqueous migration (F, Sr, Li, Cs, Rb, B in borates, sometimes U, Mo etc.) the values of $k < 1.0$. are to be expected. In arid zone regions for the identical conditions and elements, in the presence of evaporative accumulation, values of $k > 1.0$ may be found.

3. In humid zone regions exhibiting mild relief features and inhibited denudation for ore elements represented by heavy ($d >$ >4 g/cm^3) and weathering-resistant primary or secondary minerals (Au, Pt, Sn, W, Nb, Ta, Zr and others) we can expect values of $k > 1.0$.

4. In a profile of modern eluvio-deluvium and ancient-origin residuum the value of $k \geqslant 1.0$ varies in a vertical direction, approaching at a depth $z \rightarrow h$ its theoretical magnitude for ideal residual dispersion aureoles, $k = 1.0$. These general data on probable values of the proportionality coefficient k under particular conditions should be verified for eventual use to evaluate the discovered dispersion aureoles.

A direct method to determine the local values of k consists in comparing amounts of metal in dispersion aureoles as calculated from Eqs. (15) or (67) with those in metre percent calculated from

the results of trench and line sampling of a primary mineralization uncovered by trenches excavated along the same profiles by taking into account the displacement of aureole. Figure 39 shows an example of a similar determination of the coefficient of residual productivity of tin for landscapes of the Kavalerovsky district from the results of sampling in a prospect trench that discovered the Letnyaya and Dekabr'skaya tin ore veins of the Novogorsk ore showing. The region is composed of sandstones and aleurolites of the Lower Cretaceous, the distances apart the veins do not exceed 25 m. Along profile XI they form a common dispersion aureole with the amount of metal $M = 1.36$ m% of Sn, the total productivity of the primary occurrence being $M_p = 1.66$ m% of Sn. Having reduced these figures to the sections corresponding to the true thickness of the mineralized zone, we get:

$$k = \frac{M_{tr}}{M_{p(tr)}} = \frac{1.04 \text{ m\%}}{1.45 \text{ m\%}} = 0.72$$

Four determinations of k have been altogether made at the Novogorskii ore showing, the mean of which was $\widetilde{k} = 1.19$.

For most deposits trench sampling yields fairly reliable results for an appraisal of the proportionality coefficient k between the residual aureole and the primary mineralization. Clearly, in specific cases we may have to take into account a probable redistribution of ore elements in the oxidation zone. So, to evaluate the proportionality coefficient for secondary copper dispersion aureoles in porphyry copper deposits we must point out whether the found value of k refers to a primary mineralization with leached outcroppings uncovered by trenches, to ores of a secondary sulphide enrichment zone, or to lean primary ore occurrences into which prospecting boreholes have been sunk.

In terms of morphology and modes of occurrence, most advantage for the evaluation of the coefficient of productivity k is offered by steeply inclined orebodies of simple shape that are sufficiently extended and display a fairly uniform strike and dip, which have steady local values of k. For orebodies of substantial thickness, e.g. stockwork deposits of isometric form $(2p_{xy} \gg 4\sigma)$ the value of the coefficient of productivity k becomes exactly equal to the ratio between the metal *content* in the region of a flat peak $\overline{C}_{max}$ of the dispersion aureole, on the one hand, and the primary mineralization, on the other hand (see Fig. 35). In all other cases where the metal content in the secondary aureole is governed by the P/σ ratio, to evaluate k we should calculate *the amount* of metal in metre percent. Added data on the value of k are provided by comparing M with M_p referred to prospecting boreholes or underground workings uncovering primary ores below the oxidation zone. Such comparisons may

(a)

(b)
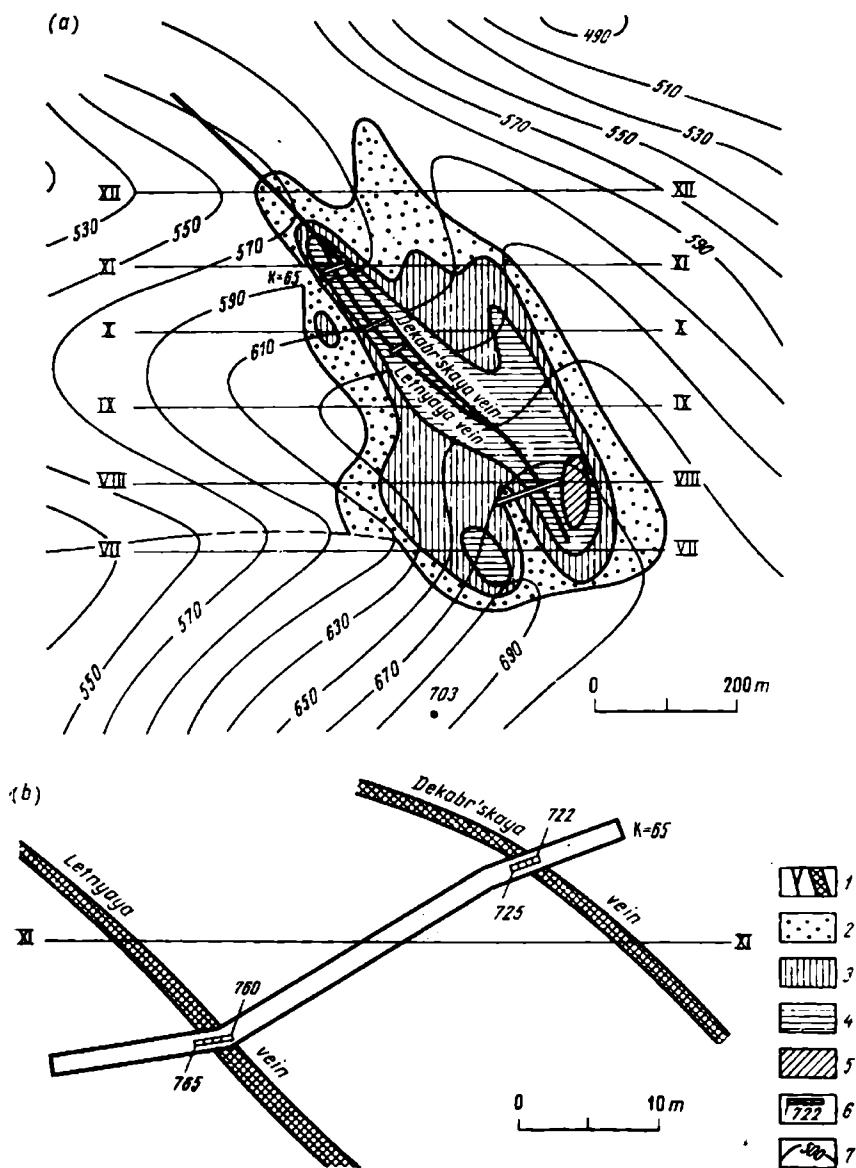
FIG. 39. Estimation of coefficient of residual productivity k on profile XI of the Novogorsk ore showing. After P.A. Kurshev:

a — secondary Sn dispersion aureole ($M_{tr} = 1.04$ m % Sn); b — plan of prospecting ditch K-65. 1 — ore veins. Tin content in eluvio-deluvium (in %): $2-1\times10^{-3}-2\times10^{-3}$; $3-2\times \times10^{-3}-6\times10^{-3}$; $4-6\times10^{-3}-20\times10^{-3}$; $5-20\times10^{-3}-60\times10^{-3}$; 6 — groove samples and their sequence numbers; 7 — isohypses.

For the Dekabr'skaya vein $M_{tr} = 0.25$m % Sn, for Letnyaya vein $M_{tr} = 1.2$ m % Sn

be made for lodes of simple shape for which the value of M_p is uniform throughout the dip and the strike.

A better characteristic of the coefficient of productivity k is obtained from a study of its value by sampling on a vertical section of aureole. By collecting detailed samples at different depths from the ground surface and calculating the amount of metal M at each horizon, it is possible to plot a graph of $M_z = f(z)$. Figure 40 provides an illustration of M_z variation and, consequently, k_z, with
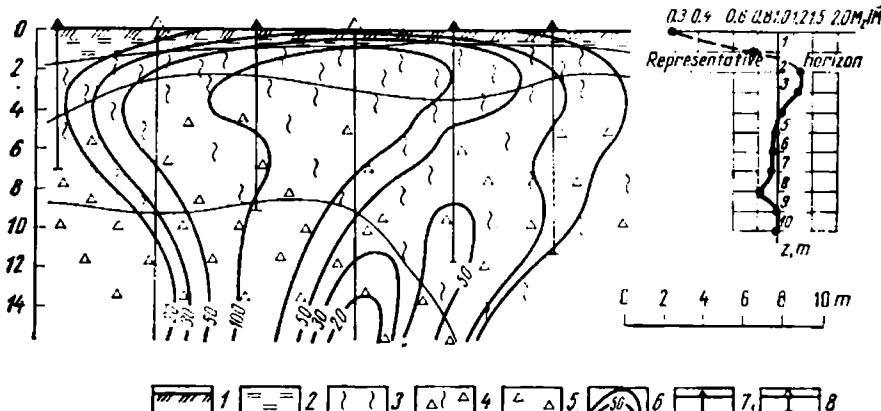
FIG. 40. Vertical cross section of a dispersion aureole and $M_z/\overline{M}$ graph:
1 — soil and vegetation cover; *2* — clays. Ancient weathering crust; *3* — clayey; *4* — clayey rock debris; *5* — rock debris; *6* — gamma-activity isolines in conventional units. Boreholes: *7* — auger drilling; *8* — core drilling

depth on a vertical section of an uranium secondary dispersion aureole. Aureole is here noticeably decayed, probably, owing to transport of allochthonous material, manifesting values of $<0.3\overline{M}$. At a depth of 2-3 m one may observe some accumulation of metal, of about 1.3 $\overline{M}$, probably, owing to its supergene leaching from the upper horizons. From a depth of 4 to 10 m the values of M_z remain, in fact, constant, notwithstanding a complicated configuration of secondary dispersion aureoles formed by two ore zones which begin to be separated at a depth 14 m as the value of σ_z decreases. At a depth 8 m the value of M_z is seen to drop to $0.82\overline{M}$ which may be due to a continuous stand of the modern watertable. Data obtained by column drilling validate the approximate value of $k \approx 1$ in the interval of steady values of M_z.

Lenticular orebodies with frequent alternating twitches and bulges spaced at intervals less than 2σ are disadvantageous for the evaluation of the proportionality coefficient k referred to prospecting trenches. The values of k_l in a homogeneous landscape connected with the non-uniform pattern of mineralization may vary by a factor

of ten or twenty. This is due to the dispersion of metal along the strike of the ore zone, as a result of which metal is transported to secondary aureoles above the twitches from the bulges and concurrently the aureoles above rich intervals of the mineralization are impoverished. A negative ranking correlation between M_p and k is indicative of such conditions. In all such cases the geometrical mean of the established values of k_i does not agree with the true value of the proportionality coefficient k_{tr}. Under conditions of an appreciable negative correlation between M_p and k and of pronounced and indistinct displacements of dispersion aureoles the correct value of k may be determined from the ratios between the areal productivity of dispersion aureole and that of the primary mineralization. For a series of separate prospecting trenches from which it is difficult to evaluate the areal productivity of a mineralization the true value of k may in the first approximation be found as the ratio of the sum total of all values of M_i to that of M_{pi} from this relationship:

$$k_{tr} = \frac{\sum M_i}{\sum M_{pi}} \tag{69}$$

Table 13 presents certain values of local coefficients of residual productivity for the most important metals according to the data obtained by different authors. These values, e.g. show the obvious relationship between $\tilde{k}$ (Pb) and $\tilde{k}$ (Zn), on the one hand, and geochemical landscape conditions, on the other. For Pb in comparable landscape one can observe an increase in the proportionality coefficient $\tilde{k}$ in carbonate rocks compared with its value for silicate rocks. This is accounted for by a higher solubility of $CaCO_3$, $Ca(HCO_3)_2$ and $CaSO_4$ compared with the solubility of the same Pb compounds.

There are practically no data on the coefficients of residual productivity for landscapes of foreign countries, such that have not been uncovered in the areas occupied by the USSR, in particular, for conditions of the tropical zone and laterite weathering. Whatever the landscape, there is some minimum value, $(M_p)_{min}$, below which for local values of coefficients k and σ the secondary dispersion aureole will not be exposed at the surface. This is due to the fact that the following condition may be satisfied:

$$\frac{k(M_p)_{min}}{\sigma \sqrt{2\pi}} < C_A - C_0 \tag{70}$$

where k is likely to be other than zero. Equation (70) characterizes a transition of the residual dispersion aureole to a concealed state forming an "extremely impoverished halo" (see Fig. 28, Type V). Incidentally, all determinations of k, given minor values of M_p,

TABLE 13

Local Values of Coefficients of Residual Productivity k

Region	Geochemical landscape	Country rocks	Chemical element	n	$\tilde{k}$	$\varepsilon \pm 1$
Zailiisky Alatau	Alpine meadow — Alpine flat watersheds of humid zone	Granodiorites	Pb Zn	12 6	0.07 0.32	1.41 1.68
"	Alpine meadow — flat slopes of semiarid zone	Effusive sedimentary rocks	Pb Zn	25 25	0.31 0.37	1.16 1.15
"	Steppe — steep slopes of arid zone	"	Pb Zn Mo Au	30 30 10 26	0.67 0.76 0.47 0.46	1.19 1.19 1.12 1.02
Central Kazakhstan	Arid steppes, isolated hills	Metamorphic schists effusive sedimentary	Pb	107	0.71	1.15
Ugamskii Ridge	Meadow steppe — flat watersheds of semihumid zone	Limestones	Pb	6	1.44	1.25
Rudny Altai	Mountain forest	Effusive sedimentary	Pb Zn	8 4	0.68 0.25	1.47 1.12
East Transbaikal and Far East	Mountain taiga	Metamorphic schists	Pb	25	0.8	1.05
East Transbaikal	"	"	Pb	70	0.60	1.13
"	"	Limestones	Pb	42	1.02	1.20
Sikhote-Alin Ridge	Mountain forest	Sandstones, slates	Sn	62	1.92	1.15

should be regarded as unreliable. Equation (70) refers to a vein-shaped orebody, for orebodies of major thickness $(2p_x, 2p_y > 5\sigma)$ it is simplified taking on this form:

$$k \, (C_p)_{min} < C_A - C_0 \qquad (71)$$

Here $(C_p)_{min}$ stands for such a low metal content in the primary mineralization, at which the dispersion aureole is not exposed at the ground surface if $k > 0$.

It is best to calculate the areal productivity P at uniform observation grid, by using a map with numerical results of spectral analyses of samples from Eqs. (16) or (17). If the spacing between the traverses of a survey net is variable, Eq. (16) is replaced by a more

9•

general relationship:

$$P = \sum_{i=1}^{m} \frac{y_i + y_{i+1}}{2} M_i \qquad (72)$$

where y_i is the distance in m along a normal from the first profile to the closest profile lying outside the contour of aureole for which $M_0 = 0$.

To characterize the areal productivity of aureole, instead of the variable P, m²%, it is better to use the index q expressed in tonnes of metal for a 1 m thick layer. Multiplying P by the density of rocks d, taken to be $d = 2.5$ t/m³ to make things easier, and dividing by 100 for converting per cent into tonnes of metal, we have

$$q = Pd \times 10^{-2} = P/40 \text{ t/m} \qquad (73)$$

The characterization of dispersion aureoles in terms of leaching or accumulation of metals in various genetic horizons of the soil profile in the general case is made possible only by the use of $M_z = = f(z)$, $P_z = f(z)$ graphs and k_z values. M and P values and their local k values among other traits characterize the geological estimation of ore objects due to their dispersion aureoles.

Sec. 3.7. Displacements and Deformations of Aureoles

The position of the midpoint of a secondary lithochemical dispersion aureole C_{max} agrees with the epicenter of an orebody outcrop at the surface of the bedrock provided that it exhibits a vertical dip and the ground surface is horizontal (see Figs. 39-43). In other cases the midpoint of aureole is displaced relative to the epicenter of the orebody by a distance conditioned by the elements of its occurrence, relief, thickness of friable formations, depth of a sampling and some other factors. Given a horizontal ground surface, the locus of the midpoints (axis) of a residual aureole on a vertical section of the eluvium will be found by a reconstruction of the weathered and dispersed portion of the orebody from its outcrop at the upper surface of the bedrock to its intersection with the ground surface. In the simplest case when weathering is unaccompanied by a change in the volume of the parent rock the distance from the orebody epicenter to the point C_{max} at the day surface will be found from a straightforward relationship:

$$S_\beta = h \cot \beta \qquad (74)$$

where $\beta < 90°$ is the angle of dip of the orebody.

If samples are collected some distance from the ground surface $z \leqslant h$ and involving a change in the rock volume, Eq. (74) takes on

this form:

$$S_\beta = B\,(h - z)\cot\beta \tag{75}$$

where B is the proportionality coefficient.

If weathering resulted in an increase in the rock volume, then $B < 1.0$; if it gives rise to a decrease, then $B > 1.0$. The value of $B = 1.0$ implies that the weathering has not caused any volume change.

When the angle of dip of an orebody is $\beta > 45°$ and the weathering is accompanied by a rock volume increase $(B < 1)$, the displacement
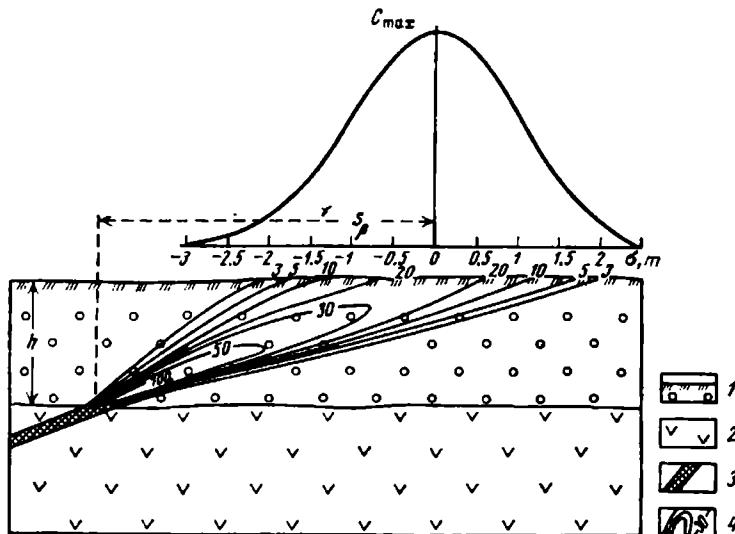
FIG. 41. Vertical cross section and graph of residual dispersion aureole at mild dip of orebody (weathering free from volume change, $B = 1$):
1 — eluvium; 2 — enclosing rocks; 3 — orebody; 4 — element isoconcentration contour lines in arbitrary units

of the central point of aureole in the direction of the rise from the projection of the primary orebody outcrop S_β will always be $< h$ and may be neglected for practical purposes. By contrast, given angles $\beta < 45°$ and weathering involving a decrease in rock volume, the displacement of aureole in the direction of the rise may attain an appreciable value of $S_\beta \gg h$. The decrease in volume is the greatest in carbonate rocks as well as in basic igneous rocks.

In temperate zones the weathering of granites occurs without a change in volume. Figure 41 shows a lithochemical dispersion aureole of a mildly inclined orebody calculated by taking into account the latter circumstance and Eq. (75).

Loose eluvio-deluvial material on a mountain slope manifesting even the slightest gradient tends to move continuously toward the foot of the slope. This movement is due to gravity and may require enormous periods of geological time to reveal itself. It is owing to the time duration that the pressure caused by the weight of the residual overburden on the slope causes inelastic deformations that are not observed at much larger but instantaneous loads. As the loose surficial materials move, they entrain dispersion aureoles developed therein, and the midpoints of aureole appear to be displaced toward the foot of the slope from the epicenters of the orebodies. That such displacements do take place is confirmed by numerous observations of orebody aureoles and is revealed by the well-known bending of the heads of steeply inclined layers on mountain slopes (see Fig. 26).

The downslope movement of the superficial loose material proceeds at a very slow rate, and, in conformity with the principle of similarity (cf. 3.5), may be regarded as a laminar flow of a liquid with an unusually great coefficient of viscosity. The movement of a plane layer of the liquid remains laminar within the limits governed by a dimensionless Reynolds number Re $\leqslant$ 700-900 found from the relationship

$$\text{Re} = \frac{h\bar{v}}{v}$$

where h is the thickness of the layer of the liquid; v is a kinematic viscosity coefficient; $\bar{v}$ is the average velocity.

For our case where v is very high, and $\bar{v}$ very small, the condition Re $\ll$ 700 is clearly observed. Laminar (non-turbulent) flow of the eluvio-deluvium is unlikely to form a dispersion aureole on the slope. This results only in a displacement of aureole without a change in the dispersion halo of ore minerals in every layer of the loose material and, consequently, of the graph of aureole C_x at the surface or at a constant depth*. This conclusion which appears to be insufficiently evident stems from the law of independent movement already mentioned above. According to it mutual mobility of particles of the loose soil mass causing dispersion of ore elements is not affected by the onward movement of the ensemble of particles.

The mechanical dispersion of ore particles or diffusion of salt aureole on the slope occurs uniformly in all directions including an upslope direction and may outstrip the downslope movement of the aluvio-deluvium. This makes it possible to come to an important conclusion that peripheral portions of a residual aureole, and in specific cases its central midpoint at depth as well at the ground surface

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* The causes of the formation of asymmetrical lithochemical aureoles on concave slopes are considered in what follows and are not connected with the movement of the loose soil mass (cf. Sec. 3.9).

may be found above the primary outcrop of the orebody.

The problem of the downslope movement of the unconsolidated surficial material has a fairly rigorous analytical solution. Let us consider the behaviour of a loose soil mass on a slope with angle of inclination to the horizontal α. Let us assume the length of the slope to be sufficiently great so as to rule out the effect of its boundaries, and let us assume the orebody to be a thin vertical vein extended in direction of slope horizontal which permits one to treat the problem as a plane one. The dip of the orebody must be 90° to the slope. Let us assume the thickness of the loose mass normal to the slope h as being constant for the portion of the slope in question and take the origin of coordinates at a point which is the projection of the primary ore outcrop on the surface of the slope (Fig. 42). Each infinitely thin layer of the regolith located at depth z and moving downslope at velocity v is being acted on by two forces: (1) tangential to the surface of the slope component of the pressure of the entire regolith overlying it equal to

FIG. 42. Displacement of residual lithochemical dispersion aureole on a flat slope:
1 — eluvio-deluvium; 2 — enclosing rocks; 3 — orebody

$dgz \sin \alpha$, where d is the density of the rocks at the horizon z; g is the acceleration of gravity; (2) inversely directed force of internal friction of the medium equal to the gradient of velocity along a normal to the direction of the flow dv/dz multiplied by the coefficient of viscosity μ.

The downslope movement of the loose material occurs under conditions, such that the two forces are balanced and, consequently,

$$dgz \sin \alpha = -\mu \frac{dv}{dz} \qquad (76)$$

The value of the dynamic viscosity coefficient of the medium μ and of that of the associated kinematic viscosity coefficient $\nu = \mu/d$ are not constant quantities. Varying monotonically with depth, μ and d are the least close to the ground surface where weathering is particularly pronounced and are the largest at a depth of occurrence of the intact bedrock.

In the general case the relationship $\nu = \varphi(z)$ is unknown to us. To solve the problem, let us assume that the kinematic viscosity coefficient of the medium, as follows from what has been said above

varies with depth in conformity with the familiar hyperbolic law, in the interval $0 \leqslant z \leqslant h$ obeying the relation

$$\nu = \frac{\nu_0 h}{h - z}$$

where ν_0 is the kinematic viscosity coefficient of the upper horizon of the regolith.

This relationship illustrates the initial slow change of the properties of the medium from the ground surface downward followed by a rapid rise of ν to $\nu_{max} \gg \nu_0$, given values of z close to h. This pattern of the variation of the coefficient of viscosity of the eluviodeluvium is the most probable if we proceed from geological considerations and is in agreement with a relatively abrupt transition from the loose materials to the dense bedrocks.

Having introduced a kinematic viscosity coefficient, let us rewrite the relationship of the equilibrium condition of the rocks on the slope:

$$gz \sin \alpha = - \left(\frac{\nu_0 h}{h - z} \right) \frac{dv}{dz}$$

The division of the variables and integration of this equation yields:

$$\frac{g \sin \alpha}{\nu_0 h} \left(\frac{z^3}{3} - \frac{hz^2}{2} \right) = v + c$$

where c is the constant of integration. Its value will be found from the conditions $v = 0$ at $z = h$, whence

$$v = \frac{g \sin \alpha}{6 \nu_0 h} (2z^3 - 3hz^2 - h^3)$$

In the lapse of time T that has passed from the onset of the process till the moment of observation, any of the horizons of the regolith will have moved downslope by the value

$$S_\alpha = \int_0^T v \, dT$$

where for the conditions of an established dynamic equilibrium

$$T = T_0 \frac{h - z}{h}$$

Here T_0 is a parameter characteristic of the local conditions and, in conformity with Eq. (51), is equal to the time elapsed since the onset of weathering of a random layer of the bedrocks till the moment its weathering products have been removed by denudation agents.

By substituting $dT = \frac{-T_0}{h} \, dz$ and changing the limits of integra-

tion, we have

$$S_\alpha = \frac{gT_0}{12v_0} \sin \alpha \, \frac{h^4 - 2h^3z + 2hz^3 - z^4}{h^2} = A\chi \sin \alpha \qquad (77)$$

where $A = \frac{gT_0}{12v_0}$ is the parameter governed by the local conditions;

$\chi = \varphi\,(h,\ z)$ is the function governing the locus of the centres in each consecutive section of aureole in the regolith.

By substituting $z = 0$ into Eq. (77) we find the displacement of aureole in the superficial layer of the eluvio-deluvium relative to the projection of the primary ore outcrop at the slope plane which is important for practical purposes:

$$S_{\dot{\alpha}_0} = Ah^2 \sin \alpha \qquad (78)$$

We shall determine the shape of the curve to locate the midpoints of aureole on a vertical section of the overlying mass if we calculate the values of the polynomial χ assuming $h = 1$ and expressing z in fractions of h. Such a curve is shown in Fig. 42. In geometrical terms it represents a fourth-order parabola.

Figure 43 shows equal metal concentration lines on vertical sections of three aureoles calculated for a flat slope. The calculations used a relationship for dispersion in a thin layer with the power index of the exponent $-\frac{(x - S_\alpha)^2}{2\sigma^2(1 - z)^2}$ where S_α is found from Eq. (77) and values of the polynomial χ. The diagram is a graphic illustration of a gradual deformation of aureole with increasing the displacement amplitude of S_{α_0}.

Equations (77) and (78) characterize displacements of residual dispersion aureoles on slopes within the limits of the angles of repose. They are disturbed under conditions of rocky relief of Alpine regions during rockfalls and screes, if solifluction terraces exist and in areas where, apart from terrain degradation, linear ablation plays a dominant role giving birth to what are known as dells or flat runoff vales. The relationship between S_{α_0} and the squared thickness of the loose regolith material, and, if we allow for the local coefficient A proportional to the value of $T_0 = \frac{h}{\Delta h}$, even its cubed thickness, causes departures from an apparently direct relationship between the gradient of the slope and the amount of displacement of aureole. This stems from an increase in the thickness of the regolith and concurrent drop in the annual layer of denudation Δh at small angles α as a result of which the growth of Ah^2 may outstrip the decrease of the value of $\sin \alpha$ from steeper to flatter slopes. So, given the gradient of the country $\alpha \approx 12°$, $h = 7.0$ and $\Delta h = 0.2$ mm/yr, the value $h^3/\Delta h$ will be almost by a factor of 7 000 greater than the same index characteristic for a steep slope with the gradient $\alpha = 37°$, given $h = 0.5$ m and $\Delta h = 0.5$ mm/yr, whereas $\sin \alpha$
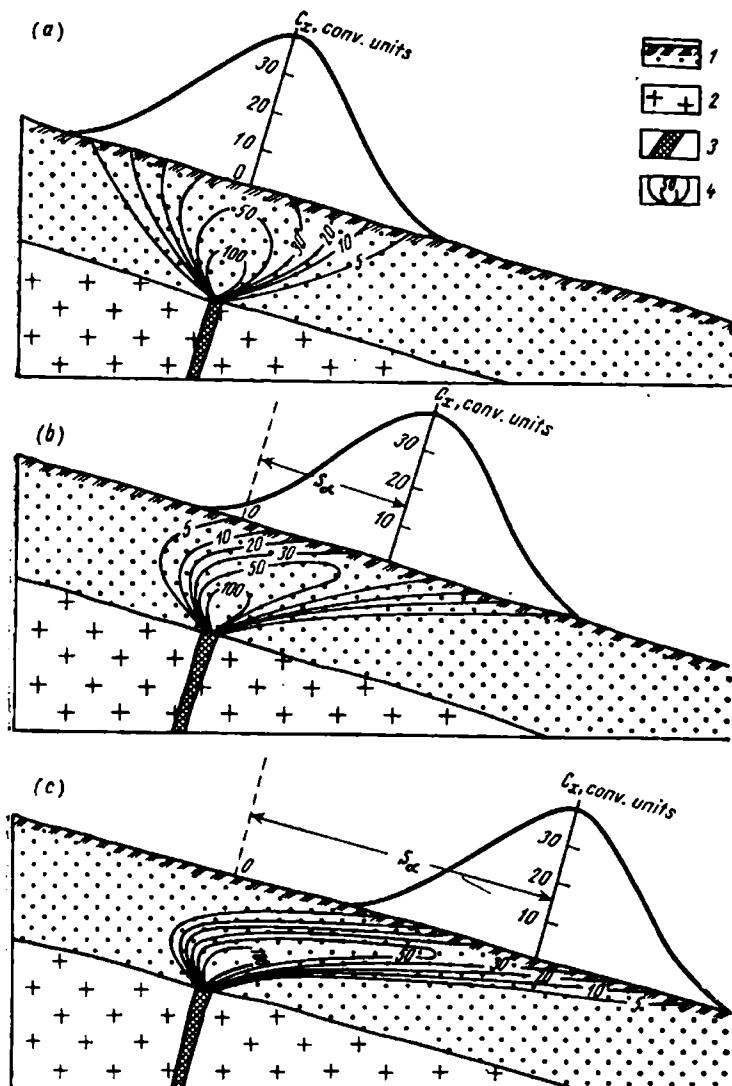
FIG. 43. Cross sections of residual dispersion aureoles (a, b and c) on slope, respectively, for various displacements: $S_{\alpha_0} = 0$, $S_{\alpha_0} = 4/3h$ and $S_{\alpha_0} = 8/3h$.

1 — eluvio-deluvium; 2 — enclosing rocks; 3 — orebody; 4 — element isoconcentration contour lines in conventional units

in this interval of angles increases only threefold. This well accounts
for the paradox of steeply dipping slopes, the absence of noticeable
displacements of secondary aureoles on very steep slopes subject
to intensive denudation. Small values of A and h, even given large
angles α, under such conditions cause only negligible displacements.
Some data on displacements of dispersion aureoles on slopes based
on our observations and on those of other authors are presented in
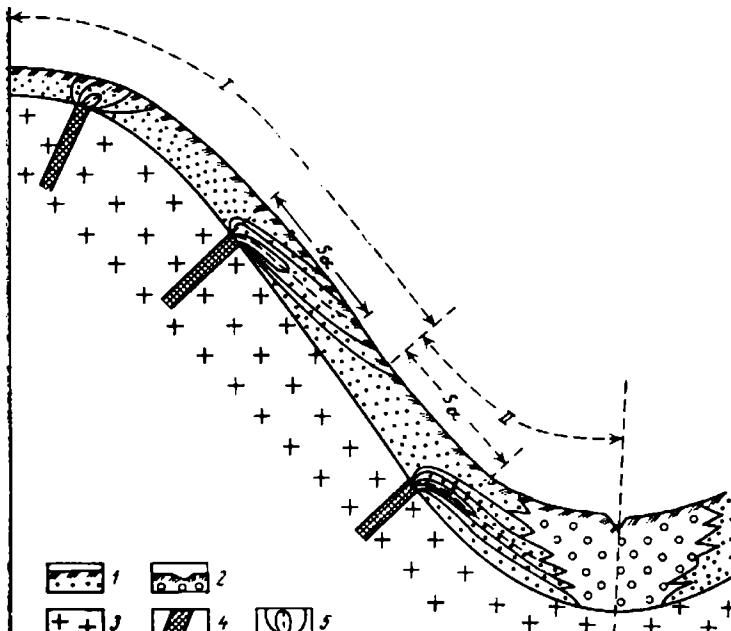
FIG. 44. Secondary residual dispersion aureole on mountainous slope:
1 — eluvio-deluvium; *2* — alluvium; *3* — enclosing rocks; *4* — orebody; *5* — secondary dispersion aureole, dashed line shows axis of dispersion aureole. Slope's intervals: I — outcropping aureoles; II — generally concealed type aureole

Table 14. Viscous plastic flow of the loose material has a result
that residual aureoles pass to a buried state at the lower portions
of slopes. Therefore, apart from the area occupied by the alluvio-
proluvial deposits in valleys along slope feet in a stretch S_{α_0} in
width, even in mountainous areas secondary aureoles of a concealed
type may develop (Fig. 44). Mountainous areas, however, manifest
intervals of open slopes frequently alternated by intervals of covered
valleys and slope feet. As has been shown by special calculations,
under such conditions, even if 75 % of the territory are covered, the
probability that major deposits may remain undetected is relative-
ly small, the decrease of targets of search is due to the discovery

of minor deposits and ore occurrences of little economic importance. It is worthwhile directing geochemical explorational effort to covered slope feet only at a stage of detailed prospecting within the boundaries of an ore field of economically important deposits. If dispersion aureole on slopes is appreciably displaced, it may be a problem to calculate the amount of metal M in the aureole on a profile and estimate the position of the central point C_{max} since the axis of the aureole in the upper layers of the loose material is almost parallel to the slope surface.

TABLE 14

Displacements of Dispersion Aureoles on Mountainous Slopes [18, 20, 24]

Region	α, degrees	h, m	S_{α_0}, m	Authors
Central Kazakhstan	5-20	0.5-2.0	Negligible	S.D. Miller, V.A. Klichnikov, et al.
Tien Shan	30-35	0.5	Absent	B.A. Dosanova, A.P. Solovov
East Trans-baikal	up to 25-30	1.0-4.0	30-50	E.M. Kvyatkovsky, I.N. Kritsuk et al. V.V. Polikarpochkin
North Transbaikal	Various	?	up to 80	M.P. Bezverkhny
Baikal Region	Various	?	up to 200	E.I. Zagoskina et al.
Ditto	up to 35	1.5-2.0	Absent	V.T. Kardash, V.K. Maslov
Buryat ASSR	Steep and moderately steep	?	250-300	V.N. Tarasov
Chukotka	4-5	2-10	up to 130-150	A.P. Solovov
East Siberia	15-18	2-3	20-30	G.S. Vakhromeev
Maritime Region	20-40	2-3	10-20	P.A. Kurshev

Equations (74) and (78) take into account separately the displacements of the dispersion aureole in the direction of the rise of the orebody S_β, given the ground surface is horizontal, and toward the foot of the slope S_α, given that the dip of the orebody is normal to the slope. In practice it is necessary to appraise the total displacement of the aureole, given that the dip of the orebody is mild and the ground surface is other than horizontal. The displacements of aureole S_α and S_β are of a directed nature and are vector quantities. Displacements are independent of one another, and the total shift of aureole S_Σ equals the vector sum

$$\vec{S}_\Sigma = \vec{S}_\alpha + \vec{S}_\beta$$

Here the resultant $\vec{S}_\Sigma$ is a diagonal of a parallelogram built on components S_α and S_β.

For conditions of a mountain slope, in Eq. (74) the meaning of the angle β is changed which must be reckoned not from a horizontal, as is usual in mining and geology, but from the surface of the slope along a line of the profile normal to the strike of the orebody, assuming that $\beta = 90°$ if the orebody is at right angles to the plane of the slope. Whenever there occurs intensive denudation of a slope covered by crushed rock, the value of the parameter B entering into Eq. (75) may be taken as equal to 1.0.

Sec. 3.8. Superimposed Dispersion Aureoles

Unlike the residual aureole formed due to the intervals of an ore zone that existed within their contour prior to the onset of weathering, secondary superimposed aureoles form in the mass of allochthonous sediments through subsequent diffusion of ore elements from depth. Even the first approximation of a mathematical solution of this problem calls for a two-dimensional problem $C_x = f\,(x,\,z)$ for values $0 \leqslant h \geqslant h_0$, where h is a distance to the orebody; h_0 is the thickness of allochthonous sediments; z is the depth of the penetration of the sampling. In lithochemical prospecting the quantitative interpretation of superimposed aureoles has not yet found universal use for there are quite a number of factors difficult to take into account that govern its efficacy. That is why we will restrict ourselves to considering the simplest model of the process.

Suppose the cover of allochthonous sediments h_0 in thickness (Fig. 45) overlies a steeply dipping sulphide. orebody subject to active modern oxidation close to the watertable located at a distance $h \geqslant h_0$ from the ground surface. Let us assume that the formation of readily solvable secondary minerals and removal of the dissolved minerals are in a dynamic equilibrium with the processes of slow denudation of the ground surface. To simplify matters, let us dispense with the effect of the capillary fringe and consider the overburden mass from the surface to the depth h as being homogeneous and isotropic in the context of the process concerned and the ground surface and watertable parallel to this latter as being horizontal. This rules out effluence of mineralized waters and permits us to restrict ourselves to analysis of a superimposed diffusion aureole (see Fig. 28, Type II). The adopted conditions are met in Fig. 45 where, in conformity with the previously considered scheme of oxidation of a sulphide deposit (see Fig. 31), a constant amount of soluble minerals is being exuded in a unit of time along the elements of a cylinder extended along the y axis. The diameter of the cylinder equal to the thickness of the orebody may be assumed to be

negligible compared with the depth of its occurrence. The ground surface bounding the diffusion makes it necessary concurrently to allow for the effect of an imaginary source which is a mirror image of the oxidizing orebody. According to V.S. Golubev, the formation of a diffusion aureole in an xOz plane owing to a linear source
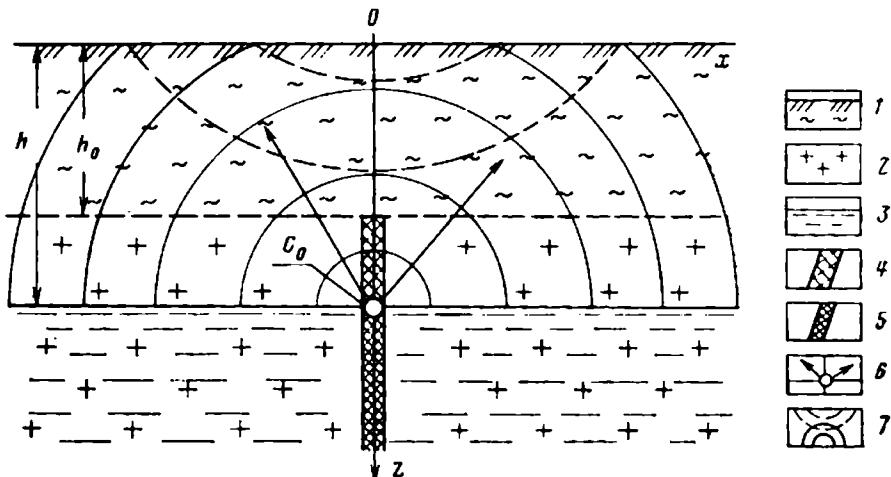
FIG. 45. Model of origination of superimposed diffusional dispersion aureole: *1* — allochthonous sediments; *2* — enclosing rocks; *3* — ground waters; *4* — oxidized ores; *5* — sulphide ores; *6* — source of ore solutions and direction of diffusion; *7* — diffusional aureole associated with actual and fictitious (dashed line) sources

parallel to the y axis in a homogeneous medium, provided there is an interface between the ground and the air, obeys this relationship:

$$C_{xz} = -\frac{\theta}{4\pi D} \left\{ \mathrm{Ei} \left[-\frac{x^2+(z-h)^2}{4DT} \right] + \mathrm{Ei} \left[-\frac{x^2+(z+h)^2}{4DT} \right] \right\} \qquad (79)$$

where θ is capacity of the orebody in kg/m·s; D is the diffusion coefficient; h is the thickness of the overburden; T is time; Ei (U) is the integral exponential function of the bracketed term whose values are tabulated in relevant handbooks.

Matters are simplified, given $z = 0$ which implies sampling on the ground surface. In this case

$$C_x = \frac{\theta_0}{2\pi D} \mathrm{Ei} \left(-\frac{x^2+h^2}{4DT} \right) + C_0 \qquad (80)$$

For small values of the term $\frac{x^2+h^2}{4DT}$ and, accordingly, large values of T, Eq. (80) may be reduced to this form:

$$C_x = \frac{\theta_0}{2\pi D} \left[\ln \left(\frac{4DT}{x^2+h^2} \right) - C \right] + C_0 \qquad (81)$$

where $C = 0.5772...$ is Euler's constant.

The graph of this relationship is a symmetrical curve with one
peak at a point $x = 0$ asymptotically approaching the geochemical
background value. Calculations made by using this relationship for
great values of T suggest a "pillar-like" shape of the superimposed
aureole in a vertical section which is not inconsistent with the avail-
able evidence. This is what makes superimposed aureoles distinctly
different from residual aureoles which, viewed in a profile, have
the shape of a fan expanding toward the ground surface (see Fig. 38).
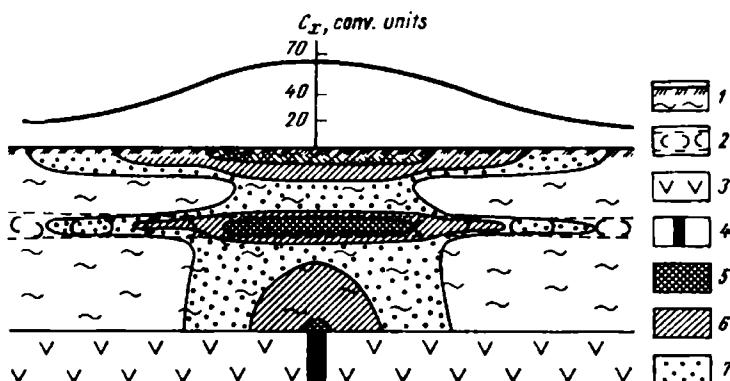
FIG. 46. Design model of superimposed dispersion aureole and [graph of terres-
trial survey:
1 — allochthonous sediments; 2 — horizon of ore element accumulation; 3 — enclosing rocks;
4 — orebody. Values of ore element concentrations given in conventional units; 5 — > 50;
6 — 30 to 50; 7 — 20 to 30

Equations (79)-(81) characterize the salt component of a litho-
chemical aureole in which the diffusing ore element is preserved in
the pellicular moisture saturating allochthonous sediments. These
soluble components may be subject to evaporational accumulation
and sorption at the ground surface and to various exchange reac-
tions on passing to a solid phase which, naturally, may cause depar-
tures from the above relationships.

Under natural conditions the formation of superimposed aureoles
is complicated by biogenic processes and flat-bedded occurrence
of the overburden layers with variable values of the diffusion coef-
ficient. In such conditions it becomes impossible to solve this prob-
lem analytically, and one must use numerical methods and comput-
ers to model superimposed aureoles.

Figure 46 is a vertical section and a graph of a superimposed au-
reole calculated for a simplified model. According to the condition,
the ore element is being accumulated close to the ground surface and
in one of the lithological horizons of sedimentary cover G.N. Za-
sukhin reports that it was possible to discover a very intensive out-

cropping diffusion aureole of Mo (and, less distinct, of Cu, Pb) over Makan copper pyrite deposit, the thickness of the overlying Jurassic sediments being up to 30 m. A superimposed aureole of Cu, Ba, Ag, Pb, Ni, Co has been revealed over copper pyrite deposit named after the 19th Party Congress (Chelyabinsk Region) with the thickness of the overlying Paleogene-Neogene and Quaternary clays varying from 15 to 75 m. According to M.A. Glazovskaya, in the Gai copper pyrite deposit an outcropping superimposed aureole of Cu some 1.5 km^2 in area with the Cu content up to 1% has been discovered 2-2.5 km south-west of lode No. 5. The overburden, 70 to 100 m in thickness, was composed of Jurassic clays, sands, conglomerates and Neogene and Quaternary loams. This unique litho- and hydrochemical anomaly is due to an outcrop of high-mineral content sulphate aqueous solutions that have given rise to what is now known as a "Vitriol lake". In contradistinction to diffusion aureoles, this must be referred to a less common type of "hydromorphic" aureoles that has been formed under conditions of mineralized water leakage being discharged into present drainage system. These facts substantiate the probability of the formation of superimposed diffusion (and more complex type) aureoles over deposits of sulphide (copper pyrite) ores even given that the cover of allochthonous sediments may be 30-50 or more than 100 m in thickness. By contrast, as manifested by the data of V.A. Bugrov, a two metre-thick layer of Neogene clays in arid desert landscapes provides an impregnable screen to Mo and W residual aureoles over a rare metal stockwork mineralization in granitoid materials and the superimposed aureole penetrates as little as 0.5-0.6 m of the cover. A.S. Milyaev and A.N. Fokin consider 3 m of the cover as being the limit thickness for the formation of outcropping superimposed aureoles of U and Mo deposits in arid steppe landscapes of North Kazakhstan. All the above data refer to the results of direct spectroscopic analyses of samples. On the whole one cannot be sure to discover superimposed aureoles over buried deposits by using standard methods of lithochemical surveys involving total analyses of samples if the thickness of allochthonous sediments exceeds a few metres.

According to the findings of Yu.N. Yushkov, lithochemical surveys involving acid extracts from samples [20] permit, under conditions of the eastern slope of the Urals, to discover superimposed diffusion aureoles of copper pyrite deposits, given the thickness of the cover 25-35 m, compared with 5-7 m when conducting bulk spectral analyses. L.V. Antropova believes it is possible to reveal superimposed dispersion aureoles above a Cu and Ni mineralization in the pre-Cambrian basement rock of the Voronezh anteclise from selectively extracted metalloorganic compounds of Cu, the thickness of the overlying Paleozoic and younger sediments being 100 to 140 m (such aureoles seem to refer to Type III). Yu.E. Saet has conducted

special studies of superimposed aureoles of buried sulphide deposits analysing acetate buffer extracts for the total metal content. According to his published findings, secondary aureoles in soils have been observed by different workers using relevant extracts, the thickness of the overburden being in the range from 8-10 to 100-130 m [28]. Weak geochemical anomalies can be also revealed by a method of extraction and analysis of thermomagnetic fractions proposed by N.A. Voroshilov and a method of partial extraction of metal (PEM). That selective (partial phase) analyses of samples can provide surface indications of secondary superimposed aureoles over buried deposits arouses, in principle, no doubt.

A direct method of increase in contrast of very weak superimposed aureoles consists in computerized handling of the results of general (bulk) analyses of samples. This method of treatment of geochemical prospecting data saves time and money and should be preferred to any selective sample analyses which are generally labour-consuming and costly.

As is known, the configuration and dimensions of weak geochemical anomalies are governed by the techniques of geochemical surveys. We may easily imagine that instead of the outer isoline of 20 conventional units which contours a superimposed aureole in Fig. 46, the same halo could have been delineated by drawing a low level isoline of 30 conventional units. Then the geochemical anomaly on a vertical section of the sedimented cover would have been divided into three separate contours: at the ground surface; at an advantageous lithologic and stratigraphic horizon; and at a depth, in the zone adjacent to the orebody. In conformity with the accepted classification, a Type II aureole would have passed to a Type III and could have been mistaken for an ore-free ("perched") anomaly. Not only is the configuration but also the likelihood of the discovery of a superimposed aureole above a buried mineralization essentially governed by the methods of prospecting.

An actually existing weak anomaly will not be revealed if its contrast characteristic is $\gamma < 1.0$ which cannot be remedied by a mere densification of the sampling grid, given rutine methods of geochemical exploration. Under such conditions the weak anomaly is masked by the noise, so to detect it we must increase the amplitude of the anomaly and decrease the noise level. This problem is of general importance in engineering and has many solutions.

The simplest means to decrease the level of random natural and man-made noise is by smoothing the data using a method of a "sliding average" with the number of points in window n close to their number in the contour of the expected weak anomaly. The regular component of the geochemical field (signal) will then retain its amplitude and the random component (noise) decreases by a factor of $\sqrt{n}$ times, as does ultimately the contrast characteristic of a weak

anomaly. Since lithochemical anomalies of ores are invariably complex, a similar increase in their contrast is achieved by a multiplication of the m element contents of the typomorphic complex. In weak anomalies increments in individual element contents are commeasurable, so the amplitude of a multiplicative anomaly is increased by about m times. At the same time, the standard deviation of the multiplicative background level, in conformity with the theorem of summation of variances increases by only $\sqrt{m}$ times, and the contrast of the multiplicative anomaly increases by as many times. As a result of the combination of multiplication and smoothing processes, the contrast characteristic of a new anomaly γ^* is $\sqrt{mn}$ times greater compared with that of the original single element anomalies γ_0, or

$$\gamma^* = \gamma_0 \sqrt{mn} \tag{82}$$

This relationship is indicative of *a probable intensity* of a weak anomaly provided that random noise factors are totally independent of one another. It is in fact greater owing to their complex correlation for different elements and to a radius of self-correlation commeasurable with the spacing of samples. By this token, we may only roughly assess the values of m and n, such that extremely weak single element anomalies with a contrast characteristic $0 < \gamma_0 < 1.0$, following multiplication and smoothing of the original data, would give rise to a new anomaly with a contrast $\gamma^* \geqslant 3.0$. In conformity to Eq. (82) and, given the specified value, we have:

$$mn = \left(\frac{\gamma^*}{\gamma_0} \right)^2 \geqslant \frac{9}{\gamma_0^2} \tag{83}$$

For $\gamma_0 = 0.4$ we find that $mn > 56$. Given multiplication of five ore elements, this condition will be approximated by smoothing that involves 15 points in a window (say, three profiles with five points in each), since $5 \times 15 = 75 > 56$. Given $\gamma_0 = 0.3$ and multiplication of contents of six ore elements, it is reasonable to assume the size of the sliding average to be 3×7 points (or more if it is not inconsistent with the size of the expected anomaly). Since γ_0 remains unknown, the above calculations may be used as guidelines only. For practical purposes it is a good plan to refer to multiple averaging with small-size windows (say, $n = 2$), use non-linear windows, optimization criterion etc. [6]. The choice of ore elements for multiplication is governed by their maximum clarkes of concentration in ores compared with the local background concentration in the materials of the sediment cover. Even elements with values of $K_k \ll 1.0$, i.e. ones that are in marked deficit in ores may enter into the denominator of a multiplication coefficient. To suppress the ore-free landscape anomalies inhibiting the discovery of superimposed

aureoles from buried ore deposits, elements other than typomorphic for the expected mineralization may also be introduced in the denominator of the geochemical factor. Yet the number and meaning of the chemical elements forming the multiplication coefficient should be carefully checked. This is illustrated by special nomograms to evaluate the usefulness of multiplication. Mere multiplication of contents of many chemical elements without taking into account their contribution to a superimposed aureole (Fig. 47) and the value of the maximum contrast of single element anomalies may only make things worse.

Following computerized handling, by the use of programs prepared by Yu.V. Shvarov, of the results of a terrestrial lithochemical survey on scales 1 : 25 000-1 : 50 000, I.F. Myasnikov revealed superimposed aureoles above buried chalcopyrite polymetallic deposits in the Rudny. or Metalliferous Altai (RSFSR), the thickness of the overburden exceeding 100 m.

FIG. 47. Nomogram for estimation of results of multiplication:

m — number of elements being multiplied; $m* \leqslant m$ — number of elements contributing to weak anomaly; $\gamma_{m*} = 1.0$; $\gamma_{m-m*} = 0$

Contents of Pb, Zn, Cu, Ag and Ba from the results of conventional spectroscopic analyses were multiplied, smoothing was executed with respect to 15-21 points in a sliding window. Aureoles were not revealed by referring to original data. Whenever expedient, the results of partial analyses of geochemical samples may be handled by the use of a computer which would increase the depth of penetration of the exploratory effort attained by the separate use of the mathematical method and selective extraction of metal.

Sec. 3.9. The Relationship Between Dispersion Aureoles and Flows

We distinguish between the following five intervals in the profile of a mountain slope (Fig. 48): I—ill-defined (flat) divide; II—convex slope; III—flat slope; IV—concave slope passing to a valley V. Depending on the local relief features only one of the intervals—convex, flat or concave—may be dominant in the profile of a slope between the divide and the valley, forming various slope types. For young-origin mountainous countries V-shaped valleys with steep flat and convex slopes are typical. For regions characterized by ancient-origin relief features gentle flat and U-shaped concave slopes approaching an equilibrium profile are more common etc.

On precipitation, a fraction of the meteoric water percolates into the rock mass. If the rate of atmospheric precipitation is in excess of percolation, the formation of a surface water layer is followed by a wave-like (pulsed) surface precipitation runoff. Depending on the volume and intensity, the surface runoff may produce various effects. Close to a flat divide line the velocity and volume of the surface water runoff may be sufficient to tear off and transport rock particles only during particularly torrential rains. This is what is responsible for a belt of retarded denudation covering interval I and part of interval II of the slope. On a steeper portion of the slope the momentum of the surface water runoff increases which facilitates the tearing off and transport of particles even at lesser rates of precipitation and gives rise to a belt of active denudation covering a portion of interval II and the whole interval III of the slope. No sedimentation of the transported material occurs at the first three intervals of the slope. This is because the mass of water m involved in the surface water runoff continues to increase from the divide line toward the foot of the slope in proportion to the horizontal length of the slope, the velocity of the runoff increasing or remaining constant. The continuous increased intensity of the surface water runoff $\frac{mv^2}{2}$ makes possible further increase of the solid load of the water as more particles are torn off from the surface of the slope. As the concave portion of the slope is being reached, the velocity of the runoff diminishes. Provided that the rate of precipitation is small, the intensity of the surface running water decreases which causes a fraction of the material being transported to be sedimented. Torrential rains increasing the amount of the runoff even in concave sections of the slope may compensate for the decreased velocity of the runoff and give rise to erosion instead of sedimentation. That is why the concave interval IV of the slope is a belt of alternated sedimentation and erosion. In a valley the surficial runoff passes to a river channel discharge (temporal or constant) in which process the material transported down the slope mixes up with the stream sediments.

FIG. 48. Generalized profile of mountainous slope:

1 — eluvio-deluvium; 2 — alluvium; 3 — bedrock; 4 — boundaries of slope intervals; 5 — boundaries of belts. Roman numerals indicate mountainous slope intervals

Over flat and convex slopes that are the most distributed, erosion occurs unaccompanied by deposition of products of weathering being washed off to the river valley. The graph of the lithochemical aureole over such slopes follows the general dispersion function preserving a symmetrical rapidly decreasing shape. As early as the distance of the midpoint of aureole equal to $\pm 3\sigma$, the metal content above the background in the zone of dispersion field drops to 1/100 of C_{max} and then becomes, in fact, equal to the background level. In
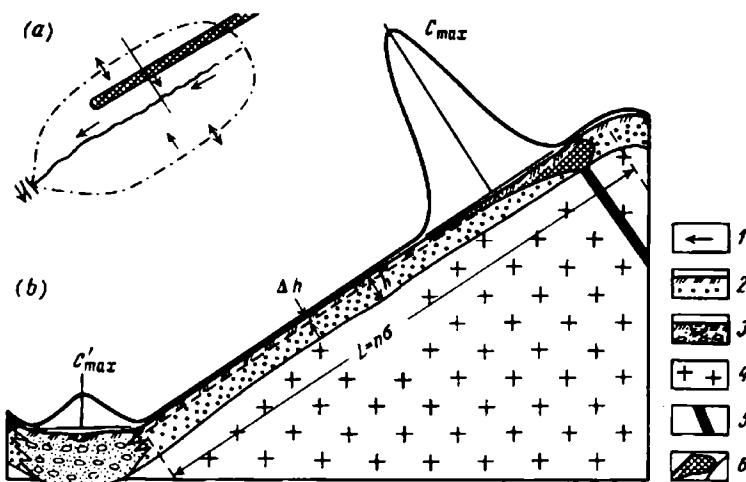
FIG. 49. Relationship between dispersion aureole and dispersion flow under conditions of flat slope of valley:

a — plan of terrain; b— cross section normal to gradient. 1 — direction of runoff; 2 — eluvio-deluvium; 3 — alluvium; 4 — bedrock; 5 — orebody; 6 — secondary dispersion aureole (3 < n < 125)

conformity with Eq. (32), the higher-than-average metal content of the dispersion flow in the alluvial material will be P/S_x on the same vertical section and may exceed the lowest anomalous value by a factor of manifold. Following the background metal contents on a slope the metal content in a dispersion flow C'_x increases again, and no continuous gradual decrease in ore element contents from the midpoint of the aureole toward an adjacent point of the dispersion flow at flat or concave slopes can be observed (Fig. 49).

Things are different if the slope profile is concave. Under such conditions the ore particles torn off from the slope in the zone of aureole may be sedimented at lower sections of the slope. In the time interval between the previous and the more vigorous subsequent action of erosion the sedimented ore mineral particles are dispersed in the mass of loose material, and the surface of the slope below the midpoint of the halo gradually, to one depth or another, attains

an anomalously high metal content. As a result, the graph of the aureole at a concave slope assumes an asymmetrical shape. The entire surface of the slope below the midpoint of aureole should then be viewed as being a region of anomalous metal contents which is intermediate between aureole and a dispersion flow (train). In lithochemical exploration it is generally called tail (train) of aureole characterizing the amount of its asymmetry. The metal content
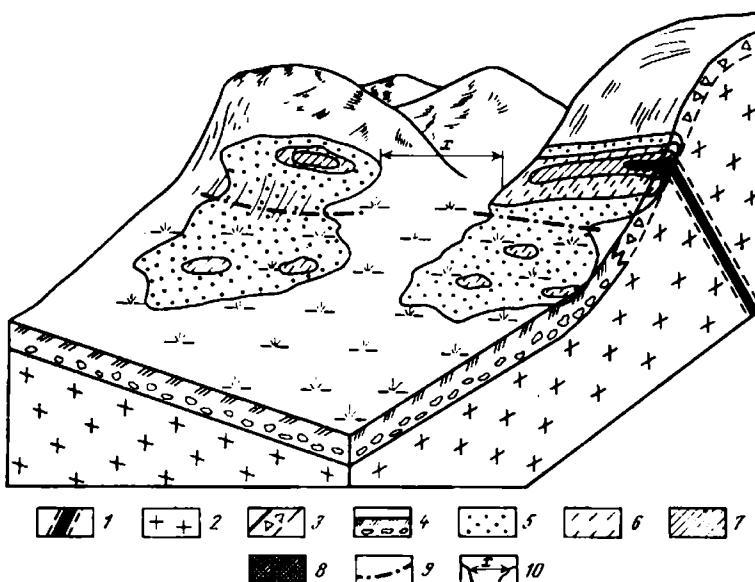
FIG. 50. Dispersion tail (train) on a concave slope:
1 — orebody and its primary halo; 2 — enclosing rocks; 3 — eluvio-deluvial formations; 4 — alluvial-proluvial sediments. Ore element isoconcentration contour lines in conventional units: 5—1 to 3; 6—3 to 10; 7—10 to 30; 8— > 30; 9 — boundary between residual dispersion aureole and its train; 10 — interval of transition of residual dispersion aureole to concealed state

within a tail gradually and non-uniformly decrease downdrainage. They may agree with the anomalous metal contents in the dispersion flow or be separated from these by a background level.

Figure 50 shows schematically typical tails of secondary orebody aureoles. A diagram is based on the actual data on the distribution of Pb as established by a 1 : 10 000 scale lithochemical survey of the Berkara District (Central Kazakhstan) [34]. If we want to assess prospective reserves or other parameters, the anomalous metal contents of tails should not be taken into account when estimating the productivity of secondary residual aureoles.

Sec. 3.10. The Solution of Direct and Inverse Problems

The direct problem of lithochemical exploration is to calculate the expected shape of a secondary dispersion aureole from the specified parameters of the orebody and local geochemical characteristics. Such a need may arise, e.g. during the evaluation of the minimum size of orebodies that can be located in a particular geochemical environment by using a given method of prospecting. This problem can be solved unambiguously.

The inverse problem is much more difficult to deal with. Its purpose is to calculate the expected parameters of an orebody responsible for the particular dispersion by referring to the characteristics of the discovered secondary dispersion aureole. The measure of success of lithochemical prospecting relies on the solution of this task. Similarly to other inverse problems, the estimated parameters of the orebody are not unique.

By knowing the thickness of the orebody $2p$ and the metal content in ore C_p as well as the local values of k and σ surmised from analogous operations in the same or similar environments, it is possible to calculate a graph of the expected secondary dispersion aureole using Eqs. (55) and (59). Then the maximum metal content, minus background, in a seam-shaped orebody constrained by the condition $2p < 2.5\sigma$ will be found from the relationship

$$C_{max} = \frac{kC_p 2p}{2.5\sigma} \tag{84}$$

The metal contents at other "specific" points of aureole, similarly to the estimation of the dispersion coefficient by a "three level method" (see Fig. 37) will be found through C_{max} from tabulated values of the dispersion function. By referring to points presented in Table 15, we may plot a complete graph of the expected dispersion aureole on one of conventional scales, given that $\sigma \approx 1.0$ cm, $C_{max} \approx 5\text{-}6$ cm.

TABLE 15

Calculations of Dispersion Aureole

Point, No.	x, m	C_x, convent. units	Point, No.	x, m	C_x, convent. units
0	0.0	$C_{max} + C_0$	1	$\pm 0.5\sigma$	$0.883C_{max} + C_0$
2	$\pm 1.0\sigma$	$0.607C_{max} + C_0$	3	$\pm 1.5\sigma$	$0.325C_{max} + C_0$
4	$\pm 2.0\sigma$	$0.135C_{max} + C_0$	5	$\pm 2.5\sigma$	$0.043C_{max} + C_0$
6	$\pm 3.0\sigma$	$0.011C_{max} + C_0$	All others	$\pm \infty$	C_0
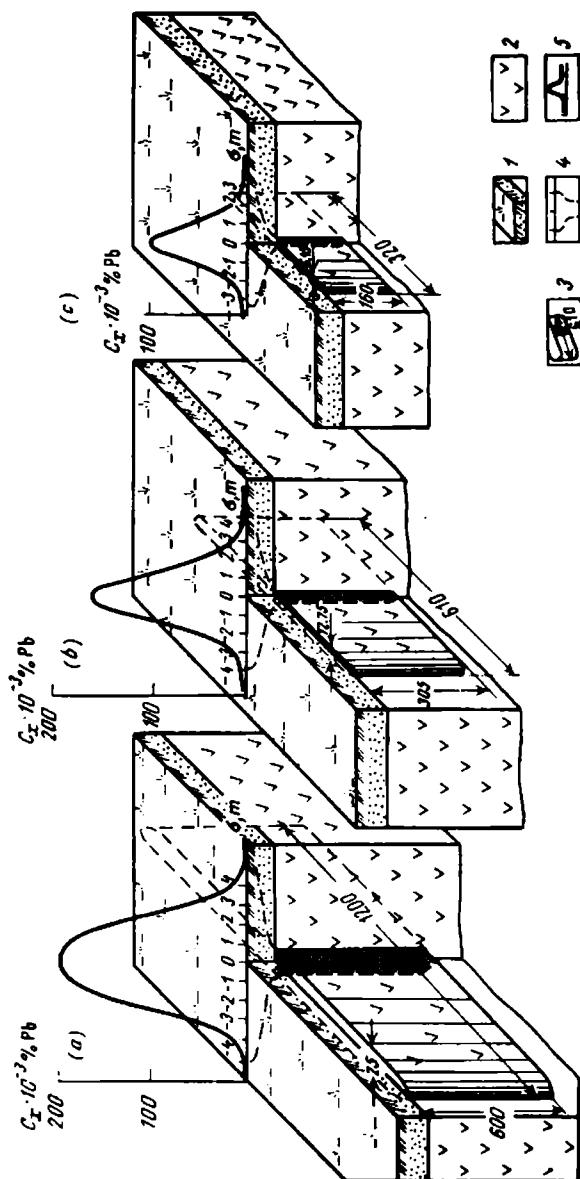
FIG. 51. Solution of direct problem for large (a), medium (b) and small deposit of Pb ores in landscapes of eroded watershed of the Zailiiskii Alatau [20]:

1 – eluvium with perfectly developed mountainous meadow soils; 2 – enclosing silicate rocks; 3 – orebody ($C_p = 2\%$ Pb, $k = 0.1$, $\sigma = 5$ m), dimensions in m; 4 – cross section of assumed contour of secondary dispersion aureole; 5 – theoretical graph of Pb tenor in dispersion aureole

For an orebody of appreciable thickness with $2p > 2.5\sigma$ the values of C_x for five or six points of one of the branches of aureole will be found from Eq. (59) by using the values of the integral of probabilities, multiplying the calculated values by k and adding C_0.

Figure 51 gives an example of such a calculation for three orebodies of different size schematically representing "principal" ore manifestations of a major, a medium and a minor Pb ore deposit in mountain meadow landscapes of ill-defined watersheds of the Zailiisky Ala Tau. As initial data the metal contents in ores equal to $C_p = 2.0\%$ of Pb (ordinary ores were taken), orebodies being in the shape of steeply dipping (lens-shaped) deposits which are geometrical similar solids for deposits of various ranking classes referred to the decimal system of classification of ore reserves. The empirically determined local coefficient of dispersion for Pb was adopted to be $\sigma = 5.0$ m and the proportionality coefficient $k = 0.1$ corresponding to weak Pb dispersion aureoles characteristic of the particular landscapes. Calculations for a major deposit used Eq. (59), for a minor one used Eq. (55) and the data of Table 15, for medium deposit used the both relationships that manifested good convergence [20]. The theoretical graph for a Pb dispersion aureole from an average deposit (see Fig. 51b) is in fair agreement with the actual secondary aureole from polymetallic Chinasylsai deposit found in the same locality. Vertical cross sections of the theoretical (a) and actual (b) secondary aureole are shown in Fig. 52 for similar relationships $M_z = f(z)$ and orebodies with a dip other than vertical. The agreement between (a) and (b) dispersion aureole is perfectly evident which provides proof of the adequately established principles of their origination.

The analytical solution of the direct problem through the use of the relations is too bulky for complex ore zones manifesting continuously varying average metal contents in ores exhibiting primary halos alternated by "barren" rock intervals. The graph of the expected secondary aureole from complex ore zone is plotted by using a special ruler designed by R.I. Dubov. A circular measuring grid designed by R.I. Dubov makes possible a detailed representation in plan of the expected dispersion aureole in terms of isoconcentration contour lines showing the particular ore manifestation [34].

The theoretically calculated graphs and dispersion isoconcentration maps allowing for the local background parameters permit the estimation of the effective size, contrast and other characteristics of aureoles needed for geochemical exploration. That it is possible to successfully solve direct problems points to the feasibility of quantitative interpretation of secondary dispersion aureoles, i.e. solution of various inverse problems. By estimating the productivity of a residual aureole allowing for the local proportionality coefficient

we may determine the amount of metal in the primary ore whether
it is found in high-grade or low-grade ores and in the primary halo
which is of much importance. That is why to estimate the discovered
dispersion aureoles it is important that the thickness of the orebody
$2p$ and the average metal percentage C_p be determined separately
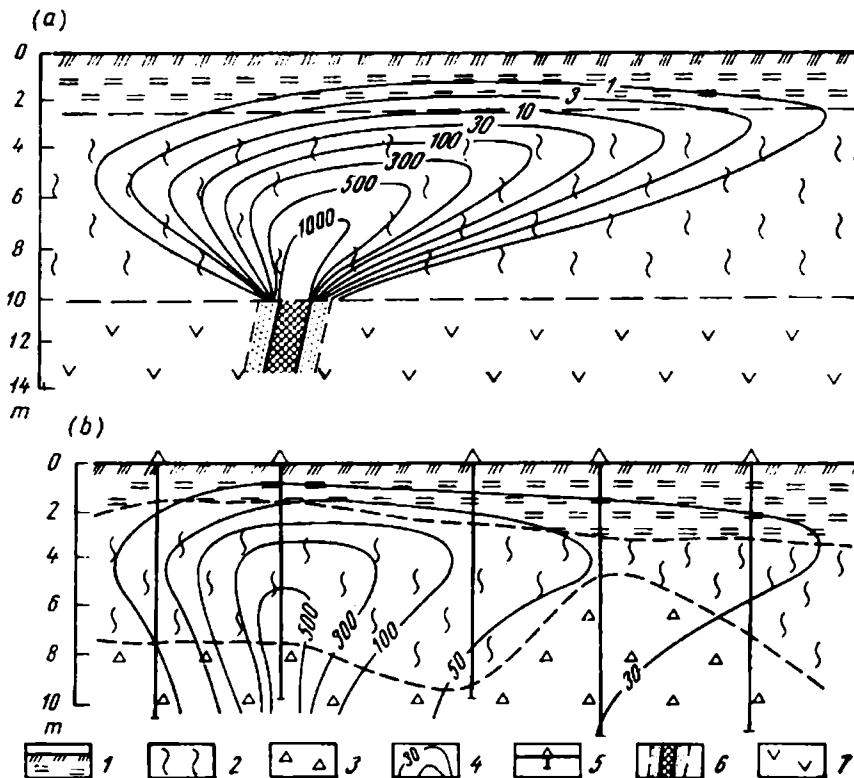
FIG. 52. Vertical cross section through design (a) and actual (b) secondary disperson aureole:
1 — overlying Quaternary sediments. Weathering crust: 2 — clayey; 3 — crushed rock;
4 — isoconcentration contour lines in conventional units; 5 — boreholes; 6 — orebody;
7 — enclosing rocks

before prospecting work is started. In conformity to "the equivalence principle", this problem cannot be solved for thin ore seams
$(2p < 2.5\sigma)$. When mineralization belts of appreciable thickness
are involved, this principle is no longer valid, and for orebodies
of simple shape it is possible to separately determine C_p, $2p$ and
σ by the use of interpretation standard curves proposed by R.I. Dubov [6].

A special nomogram was designed by Ye.M. Kvyatkovsky for numerical solution of the same problem [18]. The standard curves and the nomogram cannot be used for interpretation of graphs of complex irregular forms showing several peaks or planimetrically isometric dispersion aureoles. Quantitative interpretation of residual aureoles by using measuring grids or a nomogram is of value but it cannot substitute for trenching for ore in the primary occurrence.

The final stage of geological, geochemical and physico-mathematical interpretation of secondary aureoles is the estimation of the expected reserves of metal in the discovered mineralizations which is a measure of the efficacy of prospecting and is the principal purpose of geochemical exploration. These estimates lean heavily on analysis of the genetic type and geological and structural position of the mineralization. We will only consider here such geological and structural conditions where the evaluation of the mineralization at the surface of the enclosing rocks agrees with its estimated economic importance. Such targets of search include ore manifestations and deposits of relatively simple form that are exposed to the modern or less recent erosion surface showing economical horizons of mineralization (other than blind) of seam, lens, vein or stockwork types. The outcrops of orebodies to the surface of the enclosing rocks are more often than not overlain completely or partially by products of weathering inhibiting or preventing their direct estimation. An adequate characteristic of the size of the primary ore showing is provided by the areal productivity of its eluvio-deluvial dispersion aureole, P, $m^2\%$. By knowing the local coefficient of residual productivity k, it is possible to estimate the amount of metal (in t/m) in the primary mineralization before mining operations are started:

$$q_p = \frac{P}{40k} = \frac{1}{k}\, q \qquad (85)$$

Thus we can calculate the expected metal reserves to a depth H proceeding from the geological conditions responsible for the likely shape, level of the erosional surface and mode of occurrence of the orebody:

$$Q_H = \frac{1}{k}\, qH \qquad (86)$$

The amount of metal in a residual aureole, P, in $m^2\%$, or q in t/m is a characteristic of the mineralization outcrop in the observable stratum viewed in the plane of observation. If the depth H is reckoned normal to this plane, as follows from Fig. 53, this does not affect calculations of Q_H. If the mineralization zone has a mildly inclined dip and the depth H is measured along the dip, the value of q should be reduced to a true thickness.

The estimated reserves Q_H calculated from Eq. (86) show the total metal amount whether the rocks and ores have high or low

metal contents. On the other hand, some fraction of the metal may be concentrated outside the boundary of an economically important ore manifestation. Chapter 6 considers geological and geochemical principles of choice of reasonable depths for calculating the pros-
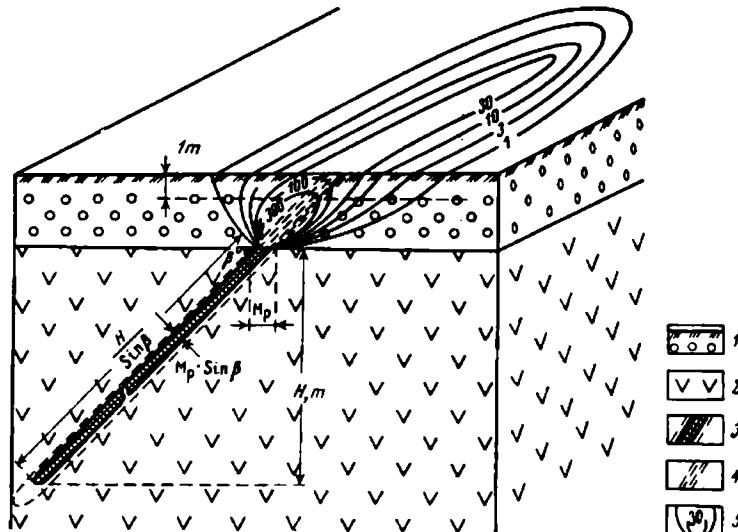
FIG. 53. Estimation of prognosticated metal reserves from secondary residual dispersion aureole:

1 — eluvium; *2* — enclosing rocks; *3* — orebody and its primary halo; *4* — orebody interval existing before weathering; *5* — metal content isoconcentration contour lines in dispersion aureole at surface and in cross section in conventional units

pective reserves and correction coefficients for converting geochemical reserves into expected economical metal reserves depending on the type of deposits. The prospective reserves estimated from the parameters of secondary residual dispersion aureoles depending on the scale of the lithochemical survey and on how well the geology of the discovered mineralization has been studied, in conformity with the data in Table 9, should be referred to P_2 or P_1 ranking classes.

Primary Halos of Ore Deposits

Sec. 4.1. An Orebody and Its Primary Halo

Each mineral deposit with an economic metal content is enclosed in space wall rocks with decreasing contents that gradually approach the local background. These concepts of the primary geochemical from mineral deposits (see Fig. 3) have taken shape relative to ore deposits and have become of most value in searching for ores. That is why we consider the theoretical premises of geochemical exploration by locating primary halos although the main principles essentially hold for prospecting for any solid mineral or, for that matter, for oil and gas. It is much easier to pinpoint new deposits if we direct geochemical exploratory effort toward a discovery of the primary halos that are much greater in area and volume compared with an economic orebody. Figure 54 illustrates the primary halo embracing a pyrite polymetallic metal deposit in the Rudny Altai. We can see that Pb, Cu and Co primary halos viewed in the plane of a prospecting profile much exceed the total area of the orebodies.

Anomalies in the enclosing country rocks discovered by exploration may be of various nature and scope. A significant anomaly with economically important metal contents is generally known as an ore showing. In case of a sufficient scope, it is ranked as an economic orebody or deposit. Geological prospecting practice describes mineralizations, in a decreasing order, as a non-economic showing, an "ore point" and a "mineralogical occurrence". A lithochemical anomaly in enclosing rocks may be called a primary halo providing that it embraces or is assumed to embrace an orebody or ore deposit. The term "endogenic halo" understood to be the primary halo of an endogenic ore deposit has entered universal use. Primary halos or aureoles about exogenic (primary sedimentation) ore deposits, following the analogy, should have been termed "exogenic halos". Due to the fact that primary halos are due to ore deposition, i.e. *concentration of chemical elements*, they should not be called dispersion halos, rather, this term must be reserved for secondary (supergene) geochemical aureoles that appear following a dispersion of previously formed deposits.

The primary halo of the principal ore element within boundary of lower anomalous content is approximated by an expanded contour of
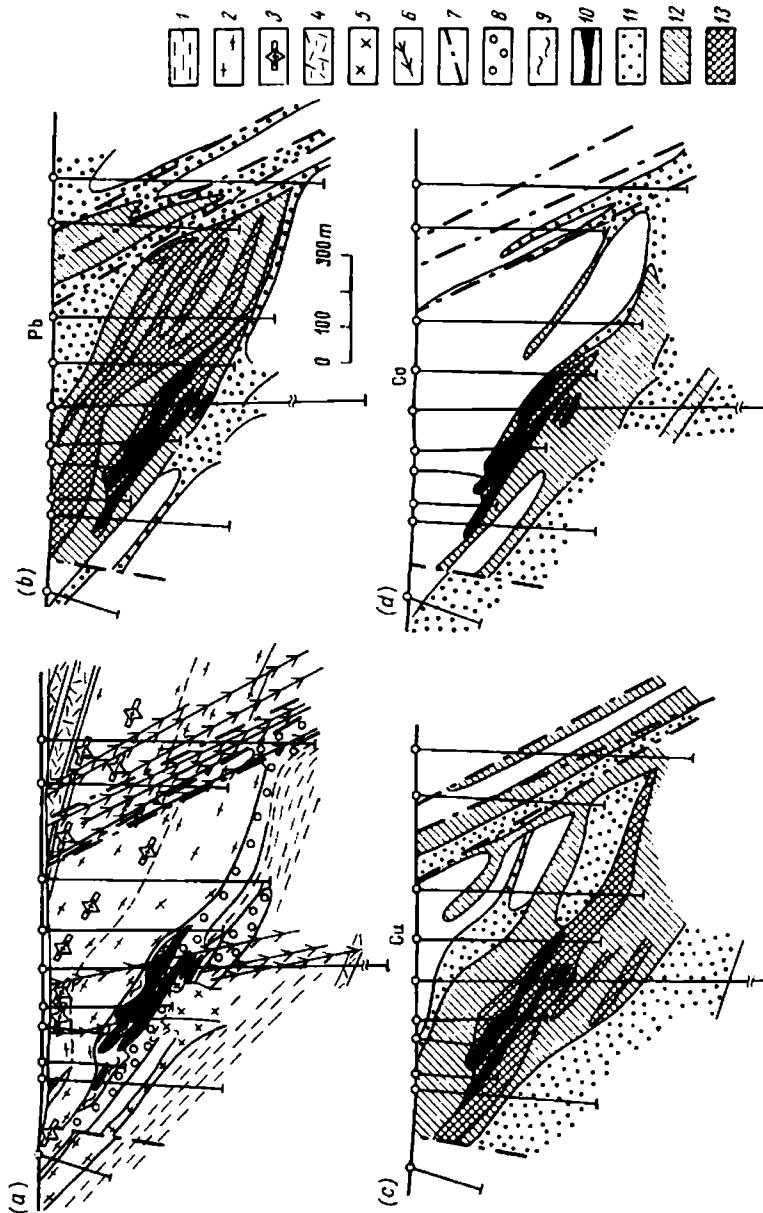
FIG. 54. Geological section (*a*) and distribution of anomalous Pb (*b*), Cu (*c*) and Co (*d*) contents in vertical cross section through central part of Zolotushinskii ore deposit [3]:

1 — sedimentary rocks; *2* — quartz porphyrys; *3* — lava brecchias of quartz porphyrys; *4* — acid composition tuffs; *5* — subvolcanic quartz porphyrys; *6* — dikes; *7* — faults; *8* — microquartzites; *9* — chloritolites; *10* — orebodies; *11-13* — primary dispersion halos in sequence of increased element concentrations (*13* — maximum concentrations)

the orebody involving departures governed by structural tectonic, magmatic and lithological and stratigraphic control of the mineralization. The contours of the primary halo of pathfinder elements that serve as guides to ore may be a larger or smaller replica of the halo embracing the principal element or, alternatively, be of an essentially different shape, e.g. be enclosed in a near-ore or supra-ore space. It can be distinctly seen from Fig. 54 that the primary Pb halos tend to be located close to the hanging side, and Co halos to the lying side of the orebody.

It is not uncommon that ore deposits that are to be economically mined do not manifest clearcut geological boundaries. Such deposits are contoured from the results of analytical data from whether it is economic to mine them, given a definite average (C_p) and minimum metal contents. Detailed prospecting for mine deposits necessarily considers five or more different average and minimum metal content values so as find the optimal variant of exploitation. Ore-bearing rocks outside the minimum-content contour are invariably referred to the primary halo of a deposit (including low-grade ores). It may be reasonable, after a lengthy exploitation of a significant deposit, to decrease the minimum economic metal content in the ores being won. Thus the size of the orebody will increase at the expense of its "primary halo". There are types of deposits where the boundary between the orebody and its primary halo is important in geological terms. For instance, aggregative sulphide ores or a quartz vein may compose a deposit the primary halo of which is developed in the enclosing rocks. However, where such orebodies wedge out along the strike, the dip or the rise, the boundary of the mineral of interest is governed by the minimum mineable thickness of the orebeds which often may be subject to revision. That is why the boundary between the ore and primary halo is invariably not of geochemical but of a temporary geological economic significance. Unless the primary halo is limited by more recent tectonic disturbances or the erosion surface, its outer boundary is equally only conventional since the chemical element contents asymptotically approach local background (cf. Chapter 1). The element contents and mineralogical composition of the ore and its primary halo essentially agree within a wide range. Clearly, a deposit contoured referring to the 0.5% metal minimum content and its primary halo with a 0.49% metal content will show the same mineralogic composition. This does not prevent a fraction of elements in ores and halos from occurring in nonmineral forms. The fact that an orebody and a halo embracing it form concurrently is not only implied by a conventional boundary between an economic and aureole metal concentration but is inferred from the term the "primary halo". Anomalous ore element contents not associated directly with an orebody but due to other causes cannot be called its primary halo.

Once a lithochemical anomaly has been discovered, it should be appraised. This is more of a problem of prospecting procedures if a borehole, prospecting trench or pit have uncovered a rich or thick orebody, although geochemical exploration is also important here. An important task of geological prospecting, where geochemistry plays an essential role, is to appraise low-grade ore showings that may serve as guides to possible orebodies. Alternative solutions that have to be considered are illustrated in Fig. 55. All the five boreholes have penetrated a mineralization zone, but only the cases *a* and *c* demonstrate low-grade mineral occurrences that deserve
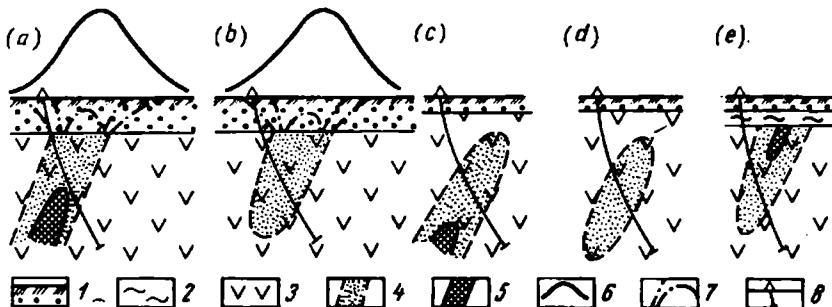
FIG. 55. Possible geological sections during occurring of boreholes of noneconomic mineralization.

Mineralization occurring at modern ground surface: *a* — primary supraore halo; *b* — dispersed mineralization zone or subore primary halo. Mineralization in concealed occurrence: *c* — primary supraore halo of hidden orebody; *d* — dispersed mineralization zone; *e* — subore primary halo from concealed deposit: *1* — eluvio-deluvium; *2* — allochthonous sediments; *3* — enclosing rocks; *4* — mineralization of noneconomic importance or primary halo (?); *5* — orebody; *6* — graph of ore element contents in supergene dispersion aureole; *7* — secondary dispersion aureole; *8* — exploratory borehole

exploratory effort directed downwards. In the cases *a* and *b* similar results could be yielded by excavating prospecting trenches or pits, analogous uneconomical ore showings are discovered during testing the walls of underground workings. A great number of showings are not primary halos from ore deposits. Most of these former are classed as noncommercial ore manifestations, zones of dispersed mineralization and ore points that much exceed in number economic ore deposits (see Table 5). Whether the discovered anomaly belongs to a supraore halo or to other horizons of the ore zone is determined following analysis of its stable geochemical characteristics taking into account the genetic type of the mineralization.

An orebody and its primary halo should be regarded as one intricately composed lithochemical anomaly—a mineralized zone with a conventionally delineated outer contour and definite internal regularities of a spatially ordered distribution of chemical elements. If we study the geochemical characteristics of the primary halo separately from its orebody we will certainly arrive at wrong

conclusions. The principles governing the inner structure of an ore zone are determined by studying, in geochemical terms, of the well explored deposits of principal economically important types of different genesis, geological structure and lithological and strati-graphic features. The numerical values of parameters of the halos and orebodies of standard deposits provide criteria for estimating lithochemical anomalies during prospecting. A science of endogenic, exogenic and metamorphogenic mineralizations intimately con-nected with a study of the formation of the primary dispersion halos has been made possible by the efforts of many workers. There is much literature concerned with ore deposit genesis. Theoretical and prac-tical geochemistry considers ore deposits as actually existing ex-ploration targets. However, to be successful, geochemical prospecting requires a knowledge of the processes responsible for ore formation. Studies of the primary halos in turn, add new evidence to the science concerned with ore deposits. The studies of the primary aureoles of endogenic deposits pioneered by N.I. Safronov have been furthered by S.V. Grigoryan [3, 4, 15] and his followers and by many others both in this country and elsewhere. Most attention has been focussed on the primary halos related to hydrothermal deposits.

It is commonly believed that the formation of ore due to hydro-thermal activity results from emplacement of metal contained in hot gaseous and liquid mineralizing fluids moving in the country rocks along weakened zones, generally from the depth upward. Transport of metal by hydrothermal fluids occurs supposedly as halide complexes, mostly $Na[MeCl_4]$ or $Na[MeCl_3]$ chlorides, some-times fluorides with hydrosulphurous complexes and CO_2 participat-ing. Ore minerals precipitate from the hydrothermal fluids following a drop in temperature and pressure as ore solutions react with the wall rock and other waters, due to changes in the pH and Eh and other conditions disturbing phase equilibria in a solution-rock sys-tem. The mineralogical and chemical zoning of a mineralization is governed by a multicomponent composition of the ore fluids and by different conditions of precipitation of individual constituents of the ore solution. All these parameters, viewed in the context of the similarity of ore and adjacent to ore metal concentrations, are mirrored in the structural and geochemical characteristics of the primary dispersion patterns from hydrothermal deposits. The de-velopment is being governed by ore controlling structures in rock strata that are advantageous for ore emplacement. The primary halos particularly agree with the assumed direction of the pressure flow (infiltration) of ore fluids—along the rise and strike of mineralized zones where the effective size of the halo may attain many hundreds of metres. Primary halos that originate from the diffusion of the solutions across the strike of mineralized zones are smaller, the effective size being sometimes a few metres only. Yet commonly

primary halos result from the joint effect of ore fluid infiltration
and diffusion embracing a vast zone of the gradually diminishing
jointing in the wall rocks. Hence a usually complicated form of the
cross section of hydrothermal deposit primary halo showing drama-
tically anomalous (infiltration-induced) ore element contents that
alternate with higher-than-average (diffusion-induced) ore element
contents (see Fig. 54).

Rather than one or two, less commonly three or four metal spe-
cies which are general useful constituents of ore deposits, geochemi-
cal exploration invariably discovers a multielement composition of
hydrothermal mineralization. What is meant is not the so-called
"occurrence" of one of the elements from the Periodical Table any
of which, according to Vernadsky's law, will be found in any rock
or ore provided that the limiting sensitivity of analysis is suffi-
cient (cf. Sec. 1.2). As many as 30 to 35 and more chemical elements
make up anomalies in the primary halos and ores in hydrothermal
deposits. This fact strongly suggests their contribution to the ore
forming process.

The primary halo of an ore deposit is a zone in the wall rocks al-
tered by hydrothermal activity. It is generally delineated by visual
estimation, less commonly from the results of analyses for K, Na, Si,
Al, Mg, Fe and other petrogenic elements whose accumulation or
subtraction occurs on seritization, quartzization, dolimitization,
hematization and other processes that accompany ore deposition.
Vast zones of altered rocks, however, may originate unassociated
with mineralization or in a preore stage and may provide only an
indirect guide to ore. What is essentially important in search for
ore are anomalous ore element contents. Primary aureole isocon-
centration lines make it possible to locate the epicentre of a blind
ore deposit.

The zoning of ore deposition, that is, the regularity in the vari-
ation of the ratio between two or more mineralization components
to the strike, dip or thickness of a mineralization is important.
W.H. Emmons was the first to consider in full detail in 1924 the
zoning of postmagmatic deposits. He pointed out a regular change
in the composition of a mineralization with depth and depending
on its location relative to the parental intrusion. He has established
sequences in the zoning of ore elements (with decreasing tempera-
ture and depth): Sn, W, As, Bi, $Au_{(1)}$, Cu, Zn, Pb, Ag, $Au_{(2)}$,
Sb, Hg [7]*. Geochemical studies of primary halos of hydrothermal

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* In a discussion that followed the zoning sequence did not evoke any
objections. J. Spurr, however, claimed priority referring to his publication
dated 1907. In response, Emmons pointed to the fact that zoning sequences had
been suggested by L. de Launay in 1900. Emmons' views were later critisized
by S.S. Smirnov. An important contribution to the study of zoning of endogenic
deposits was made by Yu.A. Bilibin and V.I. Smirnov.

deposits confirm and widen the data about series of element deposits.

A.A. Saukov first called attention to mercury as a guide to ore. Due to its chalcophilic nature and high volatility it is able to form superjacent primary halos associated with sulphide deposits of different metals. Furthering views of some elements serving as guides to ore, N.I. Safronov suggested the presence of superjacent primary halos from halides and, particularly, iodine. Later studies by V.Z. Fursov, N.A. Ozerova, M.A. Lapp, B.A. Sudov and many others corroborated these views. It is the studies by S.V. Grigoryan and L. N. Ovchinnikov [3, 15, 25] that have dealt in greatest detail with vertical zoning of the primary halos associated with hydrothermal sulphide deposits. Based on investigations of more than 300 different deposits, these workers present the following general row of element deposition zoning (from bottom upwards):

$$W_{(1)} - Be - As_{(1)} - Sn_{(1)} - Au_{(1)} - U - Mo - Co - Ni - Bi -$$
$$W_{(2)} - Au_{(2)} - Cu_{(1)} - Zn - Pb - Sn_{(2)} - Ag - Cd - Au_{(3)} -$$
$$Cu_{(2)} - Hg, \quad As_{(2)}, \quad Sb - Ba$$
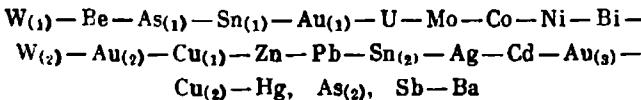
The indices 1, 2, 3 of the chemical element symbols mean that the elements may occupy different positions in the zoning sequence depending on the mineral forms and associations. So, e.g. $Sn_{(1)}$ suggests tin deposition as cassiterite SnO_2; and Sn_2 as a lower temperature stannite Cu_2FeSnS_4; $As_{(1)}$ corresponds to deposition of arsenopyrite $FeAsS$, and $As_{(2)}$ to that of orpiment As_2S_3; $Cu_{(1)}$, of chalcopyrite $CuFeS_2$, and $Cu_{(2)}$ of tetrahedrite $3Cu_2S \cdot Sb_2S_3$. The authors rightfully suggest a statistical data of the zoning sequence since in each particular deposit, depending on its genesis, one kind of substitution or another may be found which does not disturb the general sequence. The right-hand side of the above sequence may be added to by such extremely volatile elements as Tl, I; definite positions are there occupied by Th, TR, Sr, B, Li, F. Of 35 to 40 principal indicator elements L.N. Ovchinnikov selects eight "through" elements—Cu, Zn, Pb, Co, Ni, Sn, Mo, Ba—which give rise to the primary halos of endogenic deposits of most genetic types. Seven chemical elements—Sc, Ti, Cr, V, Sr, Y, Zr—are typical constituents of the primary halos from deposits associated with lithophilic metals (rare earth pegmatites, greisen, apogranite etc.) and siderophilic metals. Five elements—Be, Na, K, Bi, W—are involved in primary halos associated with lithophilic deposits and a vast chalcophilic deposit group including sulphide-containing gold ore, rare metal and fluorite deposits. Aureoles of many deposits may demonstrate subtraction of iron followed by zones of bleaching, as well as of iron group elements—Ti, V, Cr, Sc—sometimes others [25].

Zoning of hydrothermal deposits may be complicated by a multistage pattern of ore deposition followed by metamorphism. The

existence of a general consistent regularity, however, evokes no
doubt. To account for the universal character of the zoning sequence
of element deposition, different physicochemical characteristics are
presented, including solubility constants of compounds, stability
indices of simple and complex ions at different pH and Eh values,
different mobilities of hydrated ions in solutions, crystal lattice
energy levels etc. Referring to MacKay, N.I. Safronov considered
the zoning of element deposition from hydrothermal solutions was
mainly caused by the differences in their ionization potentials the
increase in which enhances ion hydration energy and diminishes
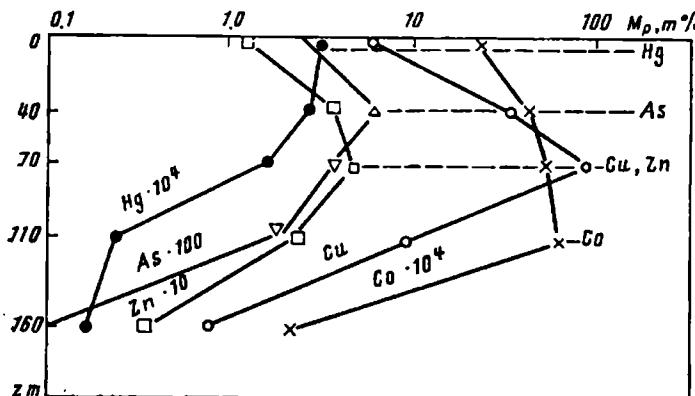
FIG. 56. Graphs of variation with depth of linear productivity of elements.
After A.S. Malakhov

its mobility. In A.A. Marakushev's opinion, zoning of mineraliza-
tion is linked with the affinity of elements to proton and sulphur.
He refers to expected sequences of deposition approaching the ob-
served ones, depending on the nature of the environment. Clearly,
deposition of ore elements from hydrothermal solutions is governed
by a number of concurrently operating factors. As rightfully believed
by L.N. Ovchinnikov, it would be no use trying to ascribe zon-
ing to one single predominant factor. It may be assumed that it is
the vast range of commeasurable factors which act jointly that are
responsible for the actually observed stability of zoning of element
deposition when fairly evident versions of particular conditions
do not change (or, if they do, then inappreciably) the ultimate re-
sult.

Vertical zoning is particularly demonstrated by steeply dipping
hydrothermal orebodies. These are mirrored by the difference in the
elevations of the maximum content depositions of individual ore
elements. Figure 56 gives examples of graphs of the linear produc-
tivity of a mineralization $M_{\text{D}} = f(z)$, characterizing the location

of these maxima. In the particular case, the zoning of element de-
position corresponds to the sequence (from bottom upward) Co,
(Cu, Zn), As, Hg, which is consistent with the universal pattern.
On the whole, ore deposition proceeds under conditions of decreas-
ing temperatures, which, for each individual element, fairly closely
approach isothermal conditions. That is why, when it is necessary
to characterize a hydrothermal ore deposit, it is worthwhile refer-
ring to "high temperature" (Sn,
W, Mo, Co etc.), "intermediate
temperature" (Ni, Cu, Zn, Pb)
and "low temperature" (Ag, As,
Sb, Hg etc.) elements and asso-
ciations which concepts have long
become accepted geological terms.

Concepts of hydrothermal ore
deposition, viewed in terms of
general geology, and the results
of studies concerned with the
primary geochemical halos make
it possible to construct a general-
ized model of primary halos of
endogenic deposits. Although it
simplifies and generalizes the
actual picture, this model essen-
tially sums up the empirical
evidence collected by various
workers. Enclosing a steeply dip-
ping body of polymetallic ores,
the principal ore elements (Pb,
Zn, Cu, Au, ...) give rise to a pri-
mary halo that roughly agrees in
shape with the orebody. Lower-
temperature pathfinder elements

FIG. 57. Model of primary dispersion
halos from hydrothermal deposit:
1 — orebody; primary halos; 2 — Pb; 3 —
Hg; 4 — J; 5 — Co; 6 — modern sediments
Roman numerals stand for sequence num-
bers of horizons

(Ag, As, Hg, ...) form primary halos shifted along the rise of the
orebody; halos from readily volatile elements (Cl, Br, I, ...) are
formed in the supraore space superjacent to the ore. In addition,
the halos from elements of a high temperature association (W, Mo,
Co, ...) are shifted in the direction of the dip from the centre of
the orebody. For other types of hydrothermal deposits, the prin-
cipal ore elements may be provided, in particular, by Sn, W, Mo,
Be; pathfinder elements of little economic importance, by Cu, Pb,
and the readily volatile constituents of a superjacent halo may in-
clude F and Li. To simplify things, the description of this model
conventionally refers to the ore element as lead, low-temperature
pathfinder element as mercury, high-temperature element as cobalt,
and readily volatile elements as iodine (Fig. 57).

If a blind orebody occurs at depth, only iodine may be responsible
for the primary halo at the ground surface and in the adjacent
horizons of enclosing rocks. At level I of the (supraore) horizon the
same iodine may give rise to two isolated anomalies located on
both sides of Hg and Pb halos. Impoverished halo Pb and Hg con-
tents may be characteristic both of horizons I and V of the mineral-
ization zone. That is why it is impossible to distinguish between
the supraore (I) and subore (V) intervals of the primary halo by the
absolute level of contents of any element. This task may be accom-
plished only by comparing ratios between the element contents.
Analysis of $M_p = f(z)$ graphs for this model shows that maximum
iodine contents were deposited above level I, mercury contents be-
tween horizons I and II, greatest lead contents correspond to horizon
III, maximum cobalt contents is located at horizon V or lower.
The position of maxima of M_p for various elements, in accord with
the above data, corresponds to this zoning sequence (from bottom
upward): Co, Pb, Hg, I. It is possible to determine the vertical zon-
ing of deposition of elements only provided that physicomechanical
and physicochemical properties of an ore zone remain constant. Any
changes in the jointing and porosity of the enclosing rocks, varia-
tions of their petrographic composition, presence in the profile of
impregnable horizons and other factors are likely to cause bulges
and pinchings in the mineralization. A great number of maxima
and minima of M_p that are due to this circumstance which occur at
the same depth for an entire group of elements mask the zoning of
their deposition. It is for this reason, that, unlike the model, in ac-
tual conditions, rather than maxima of M_p, *graphs of ratios* between
two element content values are what are responsible for their mutual
position in a zoning sequence. Apart from the natural trend for
lower temperature and more volatile elements to be located at higher
horizons of a mineralization, the superjacent halos may be enriched
by light isotopes of elements and, respectively, lower horizons may
be enriched by heavy isotopes owing to their different diffusional
mobility [30]. The superjacent primary halos from hydrothermal
deposits above the upper boundary of economically important ore
deposits, as shown by the available data, may attain the total extent
of 300-500 and even more than 1000 m.

The primary halos related to magmatic deposits proper are brought
about by liquation and crystallization differentiation of the melt
causing mineralization. It is in this fashion that syngenetic depos-
its of Cu and Ni sulphide impregnated ores are formed in the lower
portions of differentiated ultrabasic intrusive formations. The Cu
and Ni contents in economical ores of this type are up to a few per
cent, the primary halo being formed by the upper zone of impov-
erished impregnations suggestive of the incompleteness of the process
by the moment the massif solidified (Fig. 58). Vertical zoning of

metals reveals itself in the particular case as well, caused by the speedier downward movement of heavier pentlandite $(Fe, Ni)_9S_8$ $(d = 4.95$ g/cm³) compared with lighter chalcopyrite $CuFeS_2$ $(d = 4.28$ g/cm³). The primary aureoles of sedimentary, exogenic ore deposits have been studied in less detail. Genesis of several very significant stratiform copper, lead-zinc and gold ore deposits is of dubious character.

The primary halos associated with sedimented deposits manifest all the features of pre-orogenic origin, obeying lithological and stratigraphic, facial control. Under conditions of primary occurrence, these former expand horizontally or approximately so and, once there is a change in the lithological composition of the sediments, they are not traced in the overlying strata. The sedimentary ore deposits and their primary halos also display zoning characterizing a trend in the changes of sedimentation at geochemical barriers (cf. Sec. 1.8). The zoning of ore elements of sedimentary deposits is characterized by the familiar triads of N.M. Strakhov: Al—Fe—Mn for conditions of humid lithogenesis, and Cu—Pb—Zn for arid lithogenesis which illustrates the zoning of deposition of these metals as the sedimentation basin recedes from the shore line. The primary halos associated

FIG. 58. Vertical section of a magmatogenic deposit and Cu, Ni content curves:

1 — enclosing rocks; *2* — ultrabasic rocks; *3* — sulphide disseminations

with phosphorite deposits, recent or ancient alluvial and marine placers and other deposits of sedimentary genesis display peculiar features of morphology.

When delineating the contour of the primary halo of the principal valuable component it is a good plan to denote by 0.0 the beginning and by 1.0 the end of its anomalous contents reckoned along any linear direction. This scale would make it possible to find distances between two sections of a mineralization and to locate any separate intersection in the contour of a deposit. For steeply dipping orebodies the notation 0.0 marks the upper pinching out of the mineralization, the notation 1.0 corresponds to the lower pinching out of the principal component anomalous contents. These horizons (sections, levels), reckoned in the direction of the axial zoning, are known as (Fig. 59):

I—supraore, from 0.0 to 0.2;
II—upper ore, from 0.2 to 0.4;
III—middle ore, from 0.4 to 0.6;
IV—lower ore, from 0.6 to 0.8;
V—subore, from 0.8 to 1.0

which notations will be used in what follows.

The principal mineral-geochemical characteristics of deposits of the same genesis are independent of the economic scale of the mineralization and will be encountered in sections that are similarly located with respect to ore-controlling structures, channels of movement of ore material and the size of the deposit in hand. Figure 59
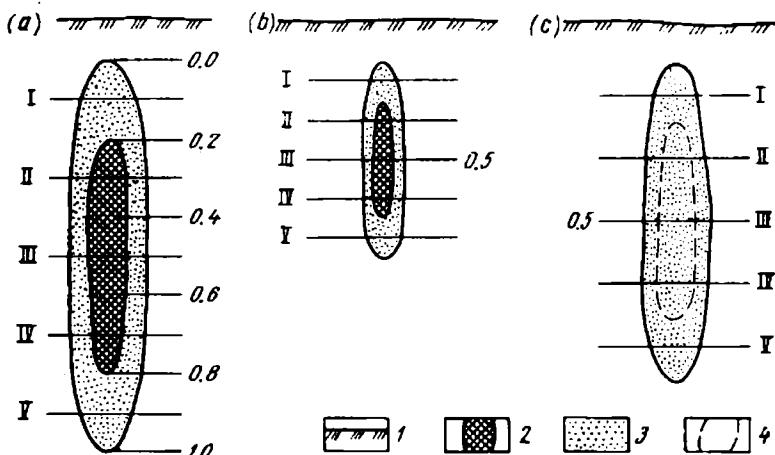
FIG. 59. Diagram showing positions of horizons in terms of the adopted metric for genetically similar ore showings:

a-b — ore showings of different size groups; c — ore showing of noneconomic importance.
1 — ground surface; 2 — high grade ores; 3 — metal contents of noneconomic importance; 4 — contour of economic ores after lowering grade standards

represents schematically three genetically similar steeply dipping lens-shaped lodes. In these, the similarity of geochemical characteristics is expected for the like horizons of the three lodes, and the differences between the depths of the horizons for each of the lodes are expected to occur. The lodes a and b, given the same quality of ores, differ in linear dimensions two times, and, consequently, in metal reserves eight times. The lodes a and c, that little differ geometrically, display, respectively, higher and lower metal content in the mineralization zone. As a result, the lodes a and b will refer to deposits of different ranking, and the lode c, to an ore showing of no economic importance. Apart from that, the regularities involved in ore deposition characteristic of the particular genetic type will

cause the geochemical features of the mineralization to vary in the same fashion with depth over the interval from the lowest to the uppermost pinchings out. It would be wrong to assume that the genetically similar lodes a and b will manifest incomparable mineral-geochemical characteristics for the mere reason that they contain different amounts of metal. In fact, it would suffice to decrease the lowest metal content in streaky impregnation ores by only 0.1%, say, for Cu; by 0.02% for Mo; or even by $1 \times 10^{-4}\%$ for Au, for a deposit of no economic importance to be ranked as a deposit with fairly large reserves. Once conditions to be met by a deposit have been reviewed, the lode c where the contour of ore is shown in a dashed line, will no longer differ from the lode a and, consequently, the previous geochemical incompatibility will disappear.

The natural geochemical properties typical of any orebody that are of genetic importance cannot originate or appear at will depending on our views as to its economic importance. If there are essential mineral-geochemical differences between an economically important and unimportant ore deposit, these should be referred to different genetic types (sub-types) for each of which the diagram in Fig. 59 will be perfectly valid. The variance of numerical values of these geochemical parameters for a series of similar sections is assumed a priori. The geochemical and geometrical similarity of genetically similar orebodies of various size, a concept of the uniformity of ore and aureole concentrations of valuable components, the tentative nature of geological and economic boundaries and estimates are essential for geochemical exploration methods.

Sec. 4.2. Parameters of a Primary Halo

Physico-mathematical analysis of ore forming processes is what adds to the description of halo of ore deposits in terms of geology. The established mathematical relationships make possible the determination of numerical values of parameters of anomalies from the observed characteristics of a geochemical field and enable the unambiguity of geological conclusions to be enhanced.

R.I. Dubov [6], V.S. Golubev [15], E.M. Kvyatkovsky [18] have proposed analytical relationships to describe the process of hydrothermal dispersion for simple physicochemical models. They all rely on a joint solution of differential equations of material balance and kinetics of heterogeneous chemical reactions allowing for some assumptions. In particular, it is most convenient to consider one-dimensional problems of ore deposition involving ore fluid infiltration along a weakened zone in the absence of diffusion

$$\frac{\partial C_{liq}}{\partial T} + U \frac{\partial C_{liq}}{\partial z} + \frac{\partial C_{sol}}{\partial T} = 0 \qquad (87)$$

and in the presence of diffusion of material from the solution into
weakly permeable wall rocks

$$\frac{U \partial C_{liq}}{\partial T} + \frac{\partial C_{sol}}{\partial T} - D\frac{\partial^2 C_{liq}}{\partial x^2} = 0 \qquad (88)$$

where C_{liq}, C_{sol} are ore material concentrations in liquid and solid
phase, respectively; T is time; U is flow velocity; D is coefficient
of diffusion; x is direction normal to the side walls of the mineral-
ization zone; z is direction along the dip of the mineralization zone.

The change in ore material concentration in the solid phase when
first-order reactions are involved can be determined from this rela-
tionship:

$$\frac{\partial C_{sol}}{\partial T} = K C_{liq} \qquad (89)$$

where K is a constant of the reaction rate which in the general case
is a function of the current coordinates.

Simultaneous solutions of Eqs. (87) and (89) or (88) and (89), giv-
en the initial and limiting conditions, make possible to characterize
the distribution of metal concentrations along the mineralization
zone and in the halo in a solid and a liquid phase, respectively, at
each individual time interval. The above references have considered
some of these solutions.

The quantitative characteristics of the process in hand require the
data on initial ore element concentrations in the liquid phase, on
the velocity of the movement of the ore fluid, its duration and pa-
rameters of the environment and reaction constants. Clearly, there
is no way to solve this problem unambiguously, since the assumed
values of one sort of quantities result in predetermined values of
the other sort of quantities, given the specified parameters of ore
deposits in hand. To decide on the method of geochemical prospect-
ing for ore deposits by locating their primary halo calls for a con-
sideration of not so much the process of ore formation as the resultant
mineralization zones manifesting ore element concentrations in the
enclosing rocks that remain unchanged in terms of our time scale
(supergene processes are not considered at this point). That is why
the symbols C_x, C_z, C_p denote in what follows ore element concen-
trations in a solid phase (C_{sol}) that are possible to directly determine,
whereas such numerous index characteristics of the ore deposition
process as C_{liq}, U, T, K etc. are regarded to be unknowns. The re-
sult of ore deposition is characterized by the numerical values of
geochemical parameters of a mineralization that can be determined
from theoretical premises and observed distributions of chemical
elements in primary halos and ores.

In the most general case ore element contents in a hydrothermal
mineralization gradually increase in the direction of ore fluid trans-

port to attain a definite level C_p corresponding to saturation conditions and to decay then gradationally since the load of the fluid will have been spent. In the elementary case in the upper and lower mineralization intervals corresponding, respectively, to the supraore and subore primary halos of the deposit the variation of metal contents with depth occurs exponentially:

$$C_z = C_p e^{-\lambda_1 z} + C_0 \qquad (90)$$

where C_p is metal concentration at points $z = 0$ at the beginning and the end of the saturation zone; λ_1 is a parameter indicative of the conditions of infiltrational ore deposition.

In a homogeneous isotropic medium metal concentrations in the adjacent diffusion-induced halo change obeying the same law:

$$C_x = C_p e^{-\lambda_2 x} + C_0 \qquad (91)$$

where C_p is metal concentration at a point $x = 0$; λ_2 is a parameter indicative of diffusion emplacement of the ore material in the wall rocks.

Equations (90) and (91), given a semilogarithmic scale of plotting, minus background, appear as straight lines with different inclinations (Fig. 60). Depending on the type of mineralization and properties of the chemical elements that are involved in the process, deposition of valuable components may occur under saturation conditions at different absolute depths of the mineralization zone and with different extents H of this interval. Maximum pathfinder element contents may be found higher or lower than the economically important ores, like those of iodine, mercury, cobalt in the halos of Pb deposit (see Fig. 57). The distribution of ore elements in a primary halo formed by the gravitational differentiation of the melt with the parameter λ_3 obeys the similar exponential law (see Fig. 58). Eqs. (90) and (91), naturally, are not the sole ones, and ore element distributions in halos and ores are often of a complex character for which analytical solutions cannot be found. The above simplest relationships fairly closely approximate the outcrops to the surface of sampling of the uppermost (apical) intervals of the supraore halo. This illustrates the most important problem, geochemical exploration for deep-seated orebodies. The parameters λ_1 and λ_2 are sometimes called "absorption coefficients" characterizing the transition of a chemical element from a liquid to a solid phase. When analysing primary halos of deposits it is better to · deal with the quantity $1/\lambda$ which has the meaning of "geochemical mobility" or "migrational capacity" of chemical elements. Since x and z are expressed in metres and the power index in the exponential equation is a dimensionless quantity, the parameter $1/\lambda$ is measured in meters which is consistent with its physical meaning. The quantity $1/\lambda_1$ is characteristic of the mobility of the chemical element in the

infiltration supraore or subore primary halo, $1/\lambda_2$ is the mobility of
the element in the diffusion adjacent halo. $1/\lambda_3$ is mobility of the
element in a magmatogenic supraore halo under conditions of grav-
itation precipitation of ore particles in the melt. In numerical
terms, the parameter $1/\lambda$ corresponds to the average path travelled
by the ore element atoms involved in the process. Being an objective
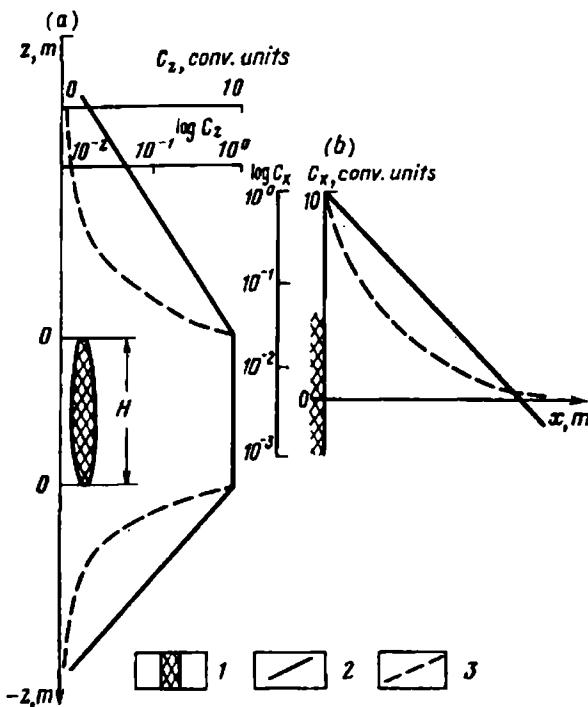
FIG. 60. Theoretical graphs of metal contents (minus background):
a — along dip of mineralized zone; b — in the adjacent halo: 1 — orebody; C_z and C_x
graphs: 2 — on semilogarithmical scale; 3 — on arithmetical scale

measure of relative geochemical mobility of elements, the parameter
$1/\lambda$ is independent of the absolute element content level, the limiting
sensitivity and accuracy of sample analyses and the effective (estab-
lished) dimensions of the halo.
    Should the graph of the observed ore element contents, minus
background, plotted in terms of coordinates x, $\log C_x$ or z, $\log C_z$
be satisfactorily approximated by a straight line, the parameter $1/\lambda$
can be determined directly. In this case cot ω of the angle of in-
clination of the averaging straight line with respect to x (or z) axis
will be directly proportional to the value of the migrational capacity

of the element. Since inclination of the straight line is governed by the chosen scale of the graph, the absolute value of the mobility of the element (in metres) will be found from this relationship:

$$1/\lambda = \frac{Y}{\ln 10} \cot \omega = 0.434 Y \cot \omega \qquad (92)$$

where Y is the adopted modulus of common logarithms of element contents expressed in a linear measure of the distance axis.
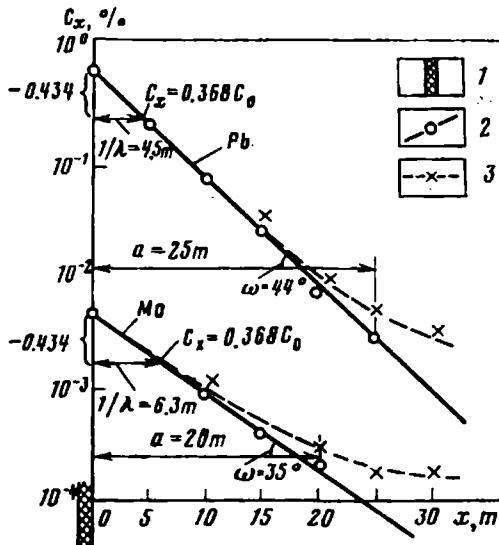
FIG. 61. Estimation of migrational capacity of elements $1/\lambda$ in diffusion-induced primary halo:
1 — mineralized zone; element content graphs: 2 — minus background; 3 — plus background.
For Pb: $C_0 = 2\times10^{-3}$ %; $C_A = 5\times10^{-3}$ %. For Mo: $C_0 = 1\times10^{-4}$ %; $C_A = 3\times10^{-4}$ %; a — effective semiwidth of halo

An example of estimation of the migrational capacity of Pb and Mo in a diffusion adjacent halo is shown in Fig. 61. The established values $1/\lambda_2$ (Pb) = 4.5 m and $1/\lambda_2$ (Mo) = 6.3 m suggest a higher mobility of Mo compared with Pb. The effective width of the primary halos from Pb exceeds that from Mo and, if we proceed from the values of non-parametric characteristics (cf. Sec. 1.5), we might come to erroneous conclusions as to the relative mobility of the elements.

Care must be taken not to confuse sequences of mobility of elements determined from the value of the parameter $1/\lambda$ with the aforementioned zoning sequences of element deposition. What was meant in the first case was the sequence of location (in terms of the dis-

tance from the ground surface, drop in temperature, remoteness from the active intrusions or the shoreline) of maximum element contents in the mineralization zone. These sequences are of a persistent character which made it possible to infer zoning sequences of element deposition for endogenic ore formation. By contrast, sequences of the migrational capacity of the elements, $1/\lambda_1$ and $1/\lambda_2$, even within the boundary of one deposit vary with depth and may even cause the coefficient of the diffusion element mobility, $1/\lambda_2$, to change in sign, forming leaching halos at deeper horizons.

If the results of analysis of samples collected from two horizons of the primary supraore halo are available, then, given that Eq. (90) is satisfied, it is possible graphically to determine the depth $z_p > z_2$ at which the metal content in the mineralization zone is expected to attain the specified value C_p. For this, it will suffice to continue the straight line through the points of log C_1, z_1 and log C_2, z_2 toward higher metal contents until it meets the abscissa C_p. A similar result will be achieved if we calculate z_p from this relationship:

$$z_p = z_2 \frac{\log C_p - \log C_1}{\log C_2 - \log C_1} = z_2 \frac{\log (C_p/C_1)}{\log (C_2/C_1)} \qquad (93)$$

where the depths z_2 and z_p are reckoned from the level $z_1 = 0$; C_1 and C_2 are the metal contents, minus background, in the midpoints of the primary halos of the first and the second level, respectively.

Whether one chemical element or another is a guide to economic ore can be fairly certainly determined from a strong positive correlation between its contents and those of the principal useful components in the halos and ores. However, *the absence of such a correlation or the statistically significant negative correlation between two element contents does not provide a proof to the deposition of the element at different stages of the process.* Indeed, if we come back to the generalized diagram of a primary halo (see Fig. 57) and assume in advance cobalt, lead, mercury and iodine to have been deposited during one stage, we may find that, apart from a strong positive correlation at definite horizons, the connection between the contents of these elements is absent, is of nonlinear character or negative. Being statistical characteristics, correlation coefficients between ore element contents have *the same values for essentially different spatial element distributions in geochemical anomalies* (Fig. 62).

Thus, the ensemble of correlation coefficients between the element contents needed for a general geochemical characteristic of ore deposits of different genesis is of no use for the identification of supraore primary halos.

Over 200 years ago the miners in the Rudny Altai region knew that with the dip of multicomponent metal deposits the lead con-

tent of ores decreased and the zinc content increased, i.e. the value
of the zoning index $\nu = $ Pb/Zn dropped with depth. Here and in
what follows, in the zoning indices ν the symbols of the chemical
elements will denote their amounts (in metre %, m^2 %) or average
contents at the horizon samples are collected from. The values of
the ratios between the element contents (or amounts), provided that
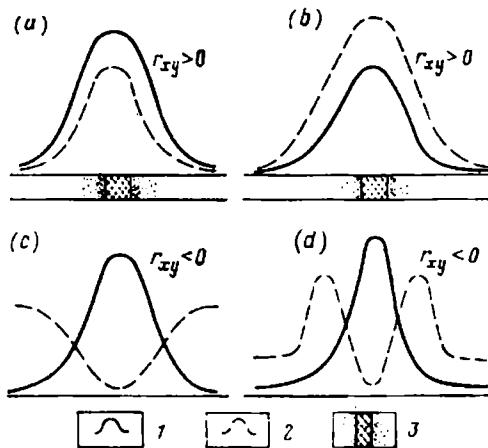
FIG. 62. Geochemical anomalies with identical coefficients of correlation between
ore element contents:
$a - x/y > 1$; $b - x/y < 1$; c and d — negative correlation for different anomaly forms.
Element content graphs: $1 - x$; $2 - y$; 3 — mineralization zone

they are *dimensionless quantities*, make it possible equally well
both to characterize a rich orebody and a mineralization of little
economic importance and to establish whether there is a similarity
or difference between them (see Fig. 59). If the mineralization at
a particular point manifests a definite value of ν, then the geochemi-
cal zoning index is provided by the spatial variation of this value,

$$\text{grad } \nu = \frac{d\nu}{dS}$$

where S is the direction in which the chosen parameter changes
the most.

Zoning is a vector quantity with orthogonal components $\frac{\partial \nu}{\partial x}$,
$\frac{\partial \nu}{\partial y}$ and $\frac{\partial \nu}{\partial z}$, where x corresponds to the direction of the true thick-
ness of the mineralization zone, y is the direction along the strike,
z is the direction along the dip of the mineralization. Clearly,

$$\frac{d\nu}{dS} = \sqrt{\left(\frac{\partial \nu}{\partial x}\right)^2 + \left(\frac{\partial \nu}{\partial y}\right)^2 + \left(\frac{\partial \nu}{\partial z}\right)^2} \tag{94}$$

One should be warned against the term zoning when what is implied is a change in the average content of any one individual element or in the thickness of the mineralization zone. It would be more appropriate to speak of an increase or decay of the mineralization, pinching out, bulge or squeeze of the mineralization zone by making use of generally accepted geological terms. Should the ratio between two chemical elements along a selected direction remain unchanged, whether the mineralization varies in morphology, is enriched or impoverished, the index is $\nu = $ const, grad $\nu = 0$, and there is no zoning in the deposition of the two elements in the given direction. Geochemical zoning is accounted for by the mineralogical zoning of the mineralization, i.e. a change in the quantitative ratios between the minerals, origination of new mineral forms or variation of the composition in the impurity elements in the minerals. That is why geochemical variation is a general characteristic of zoning of a mineralization. The most important characteristics of steeply dipping endogenic deposits are provided by vertical zoning ν_z and zoning in the plane of the orebody ν_{yz}, and for orebodies of great thickness and approaching isometric ones in the plane of a prospecting section—ν_{xz}. In the first case zoning is characterized by $\nu_z = f(z)$ graphs, in the two remaining cases by maps of isolines, respectively, $\nu = f(y, z)$ and $\nu = f(x, z)$. The zoning vector is located in these maps, whatever its position, by a normal to the isolines of ν. The primary zoning of a mineralization of interest to us is limited by a contour of known anomalous element contents $C_x > C_A$. Since indices ν are calculated with subtraction of the background, they are absent outside the mineralization zone. Regular variations of the ratios between metal contents with depth in endogenic ore deposits were reported by many workers as early as the 1930s, say, decrease with depth of the values of indices Ag/Au or Cu/As, respectively, for gold ore and copper deposits.

By referring to the value of $\nu = $ Pb/Zn, W.H. Brown has established the hypothetical paths of movement of hydrothermal fluids that gave rise to the Austinville zinc mine in Virginia. Similar studies were conducted in the Bleiklippen Mine, Greenland, by W.H. Gross. The impressive bulk of evidence he has obtained (Fig. 63) shows that in the mineralization zone at the extent of 300 m this index varies by a factor of 20 000. The map of $\nu_{yz} = $ = Pb/Zn isolines distinctly shows the position of the zoning vector corresponding to the temperature drop of quartz decrepitation.

A.D. Kablukov and G.I. Vertepov were the first to consider the ratios between the U, Mo and Pb contents characterizing vertical zoning of U deposits during geochemical exploration in 1960. The different ratios between two or more ore element contents later began to be extensively used for geochemical prospecting for blind

orebodies. The greatest resolving power permitting unambiguous identification of the mineralization zone is manifested by geochemical indices, the numerator and denominator of which are formed by the elements that occupy the extreme positions in a zoning sequence. Following from this principle, S.V. Grigoryan has selected a geochemical index for evaluating Pb-Zn deposit halos:

$$ v = \frac{Ag \cdot Pb \cdot Zn}{Cu \cdot Bi \cdot Co} $$

The numerical values of this index in a depth interval of 600 m decrease by a factor of 30 000, providing a consistent characteris-
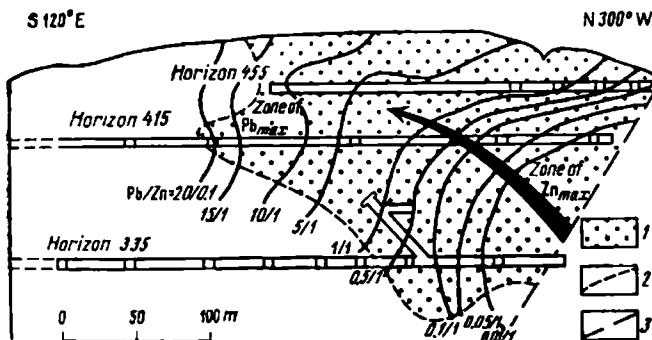
FIG. 63. Vertical profile of Bleiklippen Mine with $v = $ Pb/Zn isolines:
1 — ore; 2 — approximate boundary of ore stock; 3 — northern cross-cutting fault. Arrow shows hypothetical direction of movement of hydrothermal fluids. After W.H. Gross

tic of the investigated multicomponent metal deposits of essentially different origination conditions. Figure 64 lists geochemical indices characterizing the zoning of a copper deposit in South Kazakhstan. The value of the zoning index varies here in the interval from the supraore to the lower ore horizon (≈ 700 m) by a factor 62 million. The numerical values of such indices for deposits that have been adequately investigated are taken as reference. For the subsequent exploration to deeper horizons when doing geochemical prospecting, the anomalies with geochemical indices v approaching their upper levels are singled out. Anomalies with minor values of v which seem to refer to subore intervals, taking into account geological data, are considered to offer no promise. Geochemical zoning of referenced deposits, selection and eventual use of zoning indices are considered in more detail in the following section. What we will only point here is that, given data on the variation of zoning indices with depth, by referring to the gradient of $v_z = f(z)$ graphs, we may infer the value of the coefficient of similarity $\varkappa \gtrless 1.0$ of deposits of the

same genetic types in conformity with the relationship:

$$\varkappa = \tan \alpha_1/\tan \alpha_2 \tag{95}$$

That this relationship is substantiated in geometrical terms is illustrated by Fig. 65. Independent estimates of the coefficient of similarity in geochemical sampling of two deposits of the same type
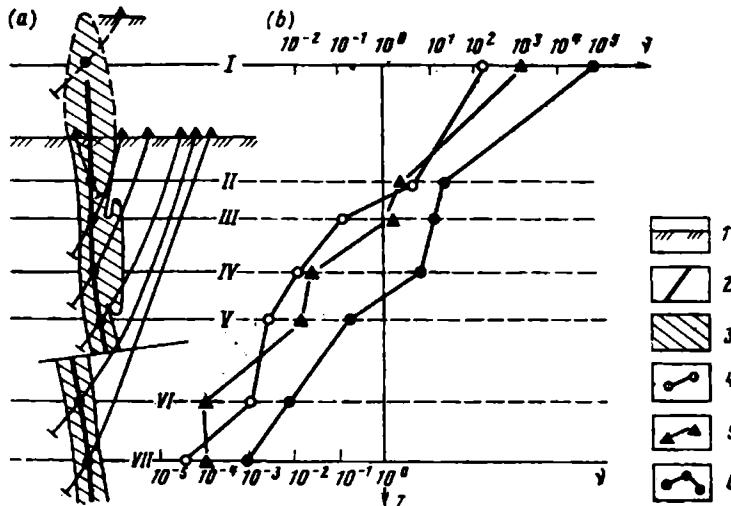
FIG. 64. Summated profile (a) and graphs of geochemical zoning indices (b) of copper ore showing:

1 — ground surface; 2 — orebody; 3 — primary halo. Graphs: 4 — $\nu = \dfrac{Pb \cdot Zn}{Cu \cdot Mo}$, $\nu_I/\nu_{VII} = 5.5 \times 10^6$; 5 — $\nu = \dfrac{Pb \cdot As}{Mo^2}$, $\nu_I/\nu_{VII} = 2.1 \times 10^7$; 6 — $\nu = \dfrac{Pb \cdot As}{U \cdot Co}$, $\nu_I/\nu_{VII} = 6.2 \times 10^7$. Roman numerals denote horizon numbers

in the interval of an economic mineralized zone deposited under "saturation" conditions or at horizons identical denoted 0.0 to 0.2 can be obtained from the relation:

$$\varkappa = (M_p)_1 : (M_p)_2 = \sqrt{(P_p)_1 : (P_p)_2} \tag{96}$$

Total metal reserves in such orebodies will be related as follows:

$$Q_1 = \varkappa^3 Q_2 \tag{97}$$

which follows from geometrical similarity of orebodies of the same type but of different size groups (cf. Sec. 1.6).

As one of parameters of a mineralized zone, N.I. Safronov has proposed to evaluate the energy of ore deposition which would permit one in comparable conventional units to quantitatively characterize multicomponent geochemical anomalies of different composi-

tion [29, 30]. Following a few simplifying assumptions, the calcu-
lation of the energy needed for ore formation uses a scheme of ther-
modynamics of isothermal compression (and rarefaction) of perfect
gas mixtures as analogy of which "barren" rocks (say, granitoids)
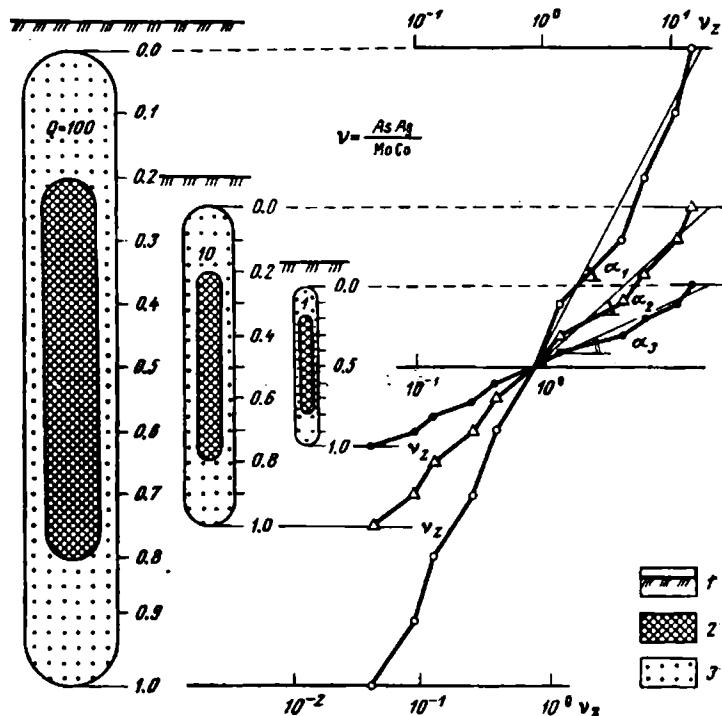
FIG. 65. Graphs of geochemical zoning indices for genetically similar deposits
of different size groups:
1 — ground surface; 2 — orebody; 3 — primary halo of principal ore component

are considered. Then energy expenditures for the formation of an ore
volume unit E for one chemical element will amount to

$$E = K_h \ln K_h. \tag{98}$$

$$E_t = \sum_{i=1}^{n} (K_h)_i \ln (K_h)_i \tag{99}$$

where E_t is the total energy of ore formation taking into account
energies of compression and rarefaction of all components of the
system.

The most straightforward and graphic relationships (98) and (99)
are analogs of the rate of decrease in entropy of a system used in

12*

the theory of information. Equation (98) implies that it is impossible for the zero element contents to exist for such a "rarefaction" would call for infinitely large energy expenditures which is substantiated by Vernadsky's law (cf. Sec. 1.2).

The relationship (99) proposed by N.I. Safronov to calculate the energy of ore formation enables one to account for the physical meaning of mutual multiplication and division of contents of two or more ore elements in multicomponent geochemical zoning indices v or for plotting multiplication halos. Since energy values are expressed through logarithms of concentrations, the multiplication and division of anomalous element contents corresponds, respectively, to the addition and subtraction of quantities proportional to the energy of their input. Consequently, in physical terms the zoning index v corresponds to the difference of energies (in J) taken for the deposition of the supraore elements entering its numerator and for the deposition of subore elements in the denominator.

Sec. 4.3. A Study of a Deposit Zonality

In geochemical exploration the most reliable criteria of the supraore primary halos, the erosion level of a deposit and expected depth of the deposit are provided by zoning indices of an ore showing. That is why it is worthwhile to consider in some detail how to obtain and eventually use these indices.

Geochemical methods of search for blind deposits and orebodies by locating their primary halos include two closely associated operations: a study of the geochemical zoning of the familiar deposits of the particular genetic type and a search for ore proper. These operations are carried out, taking into account the determined criteria, by mass "bulk" sampling of rocks, generally side walls of underground workings and cores from boreholes, in the first case sunk into known mineralized zones, in the second at the flanks and deep horizons of ore fields of the same deposits. The impressive bulk of evidence collected in the last decades permits geochemical exploration by locating primary halos and omitting the first stage of operations. However, it is necessary to study geochemical zoning of prospective and exploited economic deposits since it ensures a better understanding of their genesis, structure of the ore field and its reserves. These studies permit better accuracy in the determination of geochemical criteria of prospecting. The present section deals with the procedures of geochemical exploration solely of well known geologically (standard) deposits.

These studies basically rely on multihorizontal geochemical sampling of mineralized zones at sections spaced at intervals of 50 to 100 m, preferably on either side to reach a region with indicator element contents approaching background. Geochemical sampling is gen-

erally understood to be continuous dotted sampling of rocks and ores
by sections of 2-5 m (the mass of samples being 300-350 g) followed
by prompt analysis of these samples for 35-40 chemical elements*.
The best plan is to collect samples from the entire contour of a
standard deposit primary halo which for a steeply dipping orebody
corresponds to the interval between the supraore (I) to the subore
(V) horizonts or, in terms of the accepted notation, from 0.0 to 1.0
(see Fig. 59). This is not always feasible since the upper horizons
of a deposit may be eroded, worked out or prove inaccessible for
sampling if prospecting pits and boreholes fail to reach the subore
horizons. That is why the purpose to be achieved in practical condi-
tions is to study the deposit of interest to us by lines of geochemical
sampling. If the conditions are favourable, sampling must be carried
out outside the boundary of the primary halo of the principal
ore element, into I and Co halos to conform to the scheme in Fig. 57.
The problem of adequate geochemical sampling is considered in
what follows.

The results of sample analyses are represented as graphs and
monoelemental isoconcentration maps based on mine maps of hori-
zons and sections, generally on a 1/1 000 to 1/2 000 scale. These data
enable one to decide on the intervals for calculating the linear pro-
ductivity for vein zones (M, m%) or average ore element contents
$(\overline{C}_x\text{-}C_0)$ for isometric orebodies. The calculated results provide
initial data for analysis of zoning of the deposit under study.

The first step is to determine zoning sequences of element deposi-
tion. Appendix 26 of the acting Manual [17] for geochemical explo-
ration of ore deposits gives a detailed description of the determina-
tion of the element deposition sequence in depth.

More easily a similar result may be obtained by considering graphs
of paired ratios between linear productivities (average percentages)
of elements by levels. If the value of the ratio of two elements v
drops with depth, the element in the numerator has been deposited
above the one in the denominator. If the ratio increases, the ele-
ment in the numerator has been deposited below that in the denomi-
nator. Since graphs of paired ratios between elements may be compli-
cated in form, the z coordinates of their "centres of gravity" are cal-
culated by using this relationship:

$$z = \sum_{i=1}^{f} v_i f_i / \sum v_i \qquad (100)$$

where f_i is the sequence number of the tested horizon of the mineral-
ized zone (1, 2, 3, . . . , f); v_i are the corresponding ratios between
the productivities (average percentages) of two elements. Should the

---

* Instead of dotted sampling it is possible to select 50 g samples from dupli-
cates of geological exploration (trench) samples which is preferable.

"centre of gravity" of a graph lie above the point $\frac{1+f}{2}$, the graph appears as one decreasing with depth, if it lies below, it appears as increasing with depth. By calculating z accurate to 0.1 of a "horizon" we get 40 to 50 sites for ranging the elements.

The "centre of gravity" method makes it easy to determine the position of an additional ore element in the established zoning sequence. To do this, it will suffice to find two adjacent elements among ones that have already been considered, with one of which the new element, which enters the numerator, gives rise to a v_z graph decreasing with depth, and with the other, a graph increasing with depth.

The next step is to find the ratios between the productivities of the elements that provide unambiguous characteristics of the zoning of the mineralized zone. These requirements are best satisfied by the geochemical zoning indices v_x, v_y and v_z monotonically varying within the mineralized zone including the orebody proper and the primary halo associated with it. It has already been shown that the absolute contents of any one element are unable to characterize the zoning of a mineralization. Nor can this purpose be served by the ratios between the element contents which assume similar numerical values at different sections of the mineralized zone. Such conditions arise if the drop (or growth) of the value of v along a specified direction changes for a growth (or drop) and such irregular variations repeat. The graph of the geochemical zoning index, when we pass from one horizon to another, may have a broken form, yet the sign of its gradient should not change. The problem reduces to a consideration of different ratios between the elements so as to choose from their number the monotonically varying zoning indices. The example of a steeply dipping hydrothermal deposit is a convenient illustration of the solution of this problem.

The zoning sequence of element deposition enables one to forecast a decreasing or increasing form of graphs of v_z for the particular element pairs but fails to characterize their monotony. When looking for unambiguous zoning indices, it is better to start by analysing graphs of the ratios between two elements. Among these first-order indices monotonic v_z may be absent, their number small and the resolving power insufficient. Then one is liable to refer to second-order ($v^{II} = 2/2$) and senior-order ($v^{III} = 3/3$, $v^{IV} = 4/4$ etc.) indices whose number grows in progression and exceeds by a factor of manifold the number of paired element ratios. Geochemical indices v^{II}, v^{III} . . ., being the products of two, three or more first-order indices, respectively, correspond in physical terms to the difference of the ore formation energy for the elements in the numerator and denominator found from Eq. (99). The senior-order indices may involve one or more elements raised to the second, third or higher power until it is equal to the order of the index. In a particular case the

product of two nonmonotonic indices may vary with depth monotonically. What cannot be considered as new indices are only those that are simple power factors of junior-order indices of the type $(v^I)^2$, $(v^I)^3$, $(v^{II})^2$, $(v^I)^4$ etc.

The numbers of possible ratios from first- to third-order between the contents of 3 to 14 chemical elements are presented in Table 16. Given only 14 elements, the number of possible v runs into 100 000 which appreciably increases the probability of finding monotonically varying indices of zoning of deposits provided that the problem has been properly formulated. Clearly, one needn't consider that many ratios between element contents.

On the other hand, we cannot tell in advance which of their combinations will ensure monotony and optimum character of second- or higher-order indices. That is why joint analysis of a few hundred to over a thousand different values of v seems to be reasonable.

TABLE 16

Number of Possible Ratios Between Elements

Number of chemical elements	Order of v			Total* $\left(\frac{1}{1}\right)+\left(\frac{2}{2}\right)+\left(\frac{3}{3}\right)$
	I	II	III	
3	3	6	9	12
4	6	21	38	53
5	10	55	170	215
6	15	120	505	610
7	21	231	1 281	1 491
8	28	406	2 884	3 262
9	36	666	5 916	6 546
10	45	1035	11 265	12 255
11	55	1540	20 185	21 670
12	66	2211	34 386	36 531
13	78	3081	56 134	59 137
14	91	4186	88 361	92 456

* This column presents the number of different v without taking into account simple powers of first-order indices.

The consideration of such a great number of geochemical indices for four to five or more horizons of a mineralized zone requires the use of a computer.

The best plan to study the zoning of a deposit is by the application of the Nu-2 program prepared by V.A. Nikolaev. The geochemical field data submitted by A.A. Shiganov handled by referring to this program through the use of an EC-1022 computer are presented in Figs. 66 and 67.

CHAIR OF GEOCHEMISTRY FACULTY OF GEOLOGY, MOSCOW STATE UNIVERSITY

01.11.81   13.56   PROGRAM NU-2
                    CHOICE OF COMMON MONOTONIC ELEMENT RATIOS
DEP. YUZHNOE:(1)VEIN GLAVNAYA (LEVS. 1,2,3,4); (2)VEIN TUKENOVSKAYA (LEVS. 1,2,3);

(3)VEIN POLOGAYA (LEVS. 4,3,2,1)   TARGETS 3 (MIN. 3); ELEMENTS

CYCLES EXECUTED: 0.1111 1.1111 2.1001

```
┌─────────────────────────────┐
│    LISTING OF INPUT  DATA    │
└─────────────────────────────┘
```

01.11.81   13.56   DEP. YUZHNOE
CYCLE 0-1111
TARGET VEIN GL.
              CENTRES OF GRAVITY OF ELEMENT RATIOS IN METRIC OF LEVELS
                    ELEMENTS OF DENOMINATOR

	AU	AG	MO	PB	CO	AS	ZN	CU	AVER.
AU	2.5	1.8	2.1	1.9	1.5	1.6	1.6	1.1	1.7
AG	3.5	2.5	2.6	2.4	1.8	2.1	2.0	1.3	2.2
MO	3.6	2.4	2.5	2.2	1.6	2.0	1.8	1.2	2.1
PB	3.7	2.7	2.6	2.5	2.0	2.4	2.2	1.5	2.4
CO	3.8	3.2	3.1	3.0	2.5	3.0	2.8	1.9	3.0
AS	3.7	2.8	2.8	2.7	2.1	2.5	2.3	1.5	2.6
ZN	3.8	3.0	3.0	2.8	2.2	2.7	2.5	1.6	2.7
CU	3.8	3.2	3.1	3.1	2.7	3.0	2.9	2.5	3.1

         ZONING SEQUENCE OF ELEMENTS DEPOSITION (FROM BELOW UPWARD)

                    CU-CO-ZN-AS-PB-AG-MO-AU
                    1ST ORDER CHEMICAL ELEMENTS RATIOS
                         ELEMENTS OF DENOMINATOR

```
------------------------------------------------------------------------
! SHEET 1!     AU   !     AG    !!     CO    !    AS    !     ZN    !    CU   !
------------------------------------------------------------------------
!    !  1! 1.00E+00! 2.01E+00!!  5.73E-01! 2.59E-03! 1.34E-01! 7.26E-01!
!    !  2! 1.00E+00! 1.37E+00!!  2.95E-01! 1.43E-03! 8.80E-02! 7.33E-02!
!    !  3! 1.00E+00! 9.42E-01!!  5.75E-02! 5.90E-04! 2.52E-02! 1.44E-02!
!    !  4! 1.00E+00! 1.61E-01!!  7.12E-03! 9.28E-05! 3.16E-03! 3.02E-03!
!AU !..!............!..........!!............!..........!............!.........!
!    !  1!    •     !          •!!            !          !            !        •!
!    !  2!    •     !      •   ! !      •  !       • !       •  !      •  !
!    !  3!    •     !    •     ! !    •   !    •    !    •     !    •    !
!    !  4!    •     !   •      ! !  •      !    •    !   •      !    •    !
------------------------------------------------------------------------
!    !  1! 4.96E-01! 1.00E+00!!  2.84E-01! 1.29E-03! 6.66E-02! 3.60E-01!
!    !  2! 7.31E-01! 1.00E+00!!  2.15E-01! 1.05E-03! 6.43E-02! 5.36E-02!
!    !  3! 1.06E+00! 1.00E+00!!  6.11E-02! 6.26E-04! 2.67E-02! 1.55E-02!
!    !  4! 6.20E+00! 1.00E+00!!  4.42E-02! 5.75E-04! 1.96E-02! 1.87E-02!
!AG !..!............!..........!!............!..........!............!.........!
!    !  1! •        !      •   ! !            !       •  !         •!        •!
!    !  2! •        !          ! !      • !    •    !       •  !   •     !
!    !  3! •        !     •    ! !  •     !   •     !    •     !   •      !
!    !  4!      •   ! •        ! !  •      !    •    !    •     !   •      !
------------------------------------------------------------------------
```

         RANKING COEFFICIENTS OF CORRELATION BETWEEN ZONING SEQUENCES

                    ! TARGET !   V. GL.   V.TUK   V. POL. !
CRITICAL VALUE (5%): 0.74)   ---
                    ! V. GL. !   1   0.524   0.762 !
                    ! V.TUK. ! 0.524   1   0.214 !
                    ! V. POL. ! 0.762   0.214   1   !

    GENERAL ZONING SEQUENCE OF ELEMENTS DEPOSITION (FROM BELOW UPWARD)
                    CU-ZN-CO-AS-PB-MO-AG-AU

FIG. 66. Fragment of listing of processed results following "Nu-2" program.
Cycle 0.1111, Yuzhnoe deposit

```
01.11.81       13.57    DEP.  YUZHOE  1ST ORDER GEOCHEMICAL INDICES
CYCLE 1-1111

 I SHEET  1 I I        (AU)/(ZN)          I I        (AG)/(ZN)
 I LEVELS  I I      DECREASING            I I      DECREASING
 I TARGET   I I      NU       NU/MIN       I I      NU       NU/MIN
 I V.  GL.1  I I  1.34E-01  4.25E+01       I I  6.66E-02  3.40E+00
 I       2   I I  8.80E-02  2.79E+01       I I  6.43E-02  3.28E+00
 I       3   I I  2.52E-02  7.96E+00       I I  2.67E-02  1.36E+00
 I       4   I I  3.16E-03  1.00E+00       I I  1.96E-02  1.00E+00
 I LEVELS   I I      DECREASING            I I      DECREASING
 I TARGET   I I      NU       NU/MIN       I I      NU       NU/MIN
 I V. TUK.1  I I  4.73E-01  2.19E+01       I I  8.19E-02  6.67E+00
 I       2   I I  1.13E-01  5.23E+00       I I  4.66E-02  3.80E+00
 I       3   I I  2.16E-02  1.00E+00       I I  1.23E-02  1.00E+00
 I LEVELS   I I      DECREASING            I I  CONVENT. DECREASING
 I TARGET   I I      NU       NU/MIN       I I      NU       NU/MIN
 I V. POL.1  I I  3.17E-01  1.36E+01       I I  2.59E-02  3.03E+00
 I       2   I I  2.55E-01  1.09E+01       I I  1.30E-02  1.52E+00
 I       3   I I  5.31E-02  2.28E+00       I I  2.90E-02  3.39E+00
 I       4   I I  2.33E-02  1.00E+00       I I  8.56E-03  1.00E+00

 I LEVELS  I
 I TARGET   I I      DECREASING            I I      DECREASING
 I V. GL 1  I I            •               I I               •
 I      2   I I                            I I
 I      3   I I         •                  I I           •
 I      4   I I    •                       I I
 I LEVELS  I I
 I TARGET   I I      DECREASING            I I      DECREASING
 I V. TUK.1  I I                           I I               •
 I      2   I I           •                I I
 I      3   I I      •                     I I       •
 I LEVELS  I I
 I TARGET   I I      DECREASING            I I  CONVENT. DECREASING
 I V. POL.1  I I                           I I
 I      2   I I              •             I I               •
 I      3   I I        •                   I I
 I      4   I I      •                     I I      •

01.11.81       13.58 DEP.  YUZHNOE
CYCLE2-1001                               2nd ORDER GEOCHEMICAL INDICES

 I SHEET  1 I    (AU*AU)/(PB*AS)       I   (AU*AG)/(PB*CO)
 I LEVELS  I      DECREASING            I      DECREASING
 I TARGET   I      NU       NU/MIN       I      NU       NU/MIN
 I V. GL.1   I  1.30E-04  8.25E+02       I  1.42E-02  1.90E+02
 I      2    I  2.54E-05  1.62E+02       I  3.82E-03  5.10E+01
 I      3    I  2.16E-05  1.37E+02       I  2.23E-03  2.99E+01
 I      4    I  1.57E-07  1.00E+00       I  7.49E-05  1.00E+00
 I LEVELS  I      DECREASING            I      DECREASING
 I TARGET   I      NU       NU/MIN       I      NU       NU/MIN
 I V. TUK.1  I  2.23E-04  6.17E+01       I  3.09E-02  2.97E+01
 I      2    I  1.03E-04  2.85E+01       I  8.66E-03  8.49E+00
 I      3    I  3.62E-06  1.00E+00       I  1.04E-03  1.00E+00
 I LEVELS  I      DECREASING            I      DECREASING
 I TARGET   I      NU       NU/MIN       I      NU       NU/MIN
 I V. POL.1  I  2.33E-03  1.38E+02       I  1.76E-02  1.32E+01
 I      2    I  2.31E-03  1.37E+02       I  1.63E-02  1.23E+01
 I      3    I  2.34E-05  1.38E+00       I  3.28E-03  2.46E+00
 I      4    I  1.69E-05  1.00E+00       I  1.33E-03  1.00E+00

                    NUMBER OF 2nd ORDER RATIOS CONSIDERED  406
                    NUMBER OF COMMON INDICES 32
   JOB /NU2        / START .1356
   JOB /NU2        / STOP  .1359  CPU   2MIN 06.84SEC
```

FIG. 67. Fragment of listing of processed results following "Nu-2" program_
Cycles 1.1111 and 2.1001. Yuzhnoe deposit

A gold ore deposit called "Yuzhnoe" has been studied as a reference
one for a quartz vein type of mineralization. The enclosing rocks of
the deposit are granodiorite group intrusive rocks bursting through
the Ordovician sandy aleurolite mass. The mineralization is repre-
sented by steeply dipping and branching flat quartz veins contain-
ing native gold, pyrite, arsenopyrite and lesser amounts of other
sulphides. As can be seen from the title of the listing (see Fig. 66),
the study of the deposit zoning was started on November 1, 1981
at 13.56.

The field data included the results of horizon-by-horizon geochem-
ical sampling of three gold ore veins—the Glavnaya (4 horizons),
Tuken (3 horizons) and Pologaya (4 horizons) in the form of linear
productivities of eight typomorphic elements of the mineraliza-
tion. It was desired to determine zoning indices common for the
three ore veins which is shown in the title of the listing by "Number
of targets 3 (min 3)". Depending on the requirements of the user, the
program makes it possible to find indices that are common for m
targets from among n where $m \leqslant n$.

The data processing according to the Nu-2 program is carried
out in four cycles each of which consists of obligatory operations
and optional ones as may be needed by the user. In the given case
three cycles—zero, first and second—are executed, the latter being
included in the first and fourth operations which is indicated by two
zeros in this cycle symbol. The computer then prints a complete
table of the initial (input) data to compare it with the original copy
(omitted in the figure).

The zero cycle of the data handling is an investigation where no
previous constraints are placed on its results. For each of the tar-
gets of interest matrices of centres of gravity of paired ratios between
the productivities of the elements in the horizons metric are printed.
In so doing, the average values are presented in individual lines
basing on which zoning sequences of element deposition (from bottom
upward) are established. This is followed by printing square matrices
of the ratios between first-order elements with $v_z^I = f(z)$ graphs on
a conventionally selected scale. All the quantities and graphs in the
right-hand upper side of the matrices are repeated in reverse values
below their diagonals which is convenient for the user. Fragments
of all these data are represented in Fig. 66 showing the "Glavnaya"
vein target. The discovered sequence of element deposition, except-
ing Mo, is not inconsistent with the universal zoning sequence.
Of first-order ratios the values of Au/Ag, Au/Co, Au/As, Au/Zn, Ag/Co
and some others diminish monotonically, although the Au/Mo and
Au/Pb ratios vary irregularly. After putting out similar data for the
other two targets, the computer calculates ranked correlation coef-
ficients between the established particular sequences of element
deposition as well as the general zoning sequence from the sum of

the positions occupied by the elements in the special sequence
rows.

As can be seen from the listing, of three correlation coefficients,
only one (0.76) is significant at the five percent limit, although they
are all positive and particular sequence rows appear to be similar.
Within the limits of the available data the general sequence of zon-
ing of element deposition can be considered to have been determined.

The fact that Au is invariably present in the extreme right-hand
position in the particular sequence rows and the presence of a suf-
ficient number of continuously decreasing with depth ratios of Au
to pathfinder elements rule out the presence of a second level of
mineralization in the immediate neighbourhood of the lowest tested
horizons of the steeply dipping veins. Thus the results of the zero
cycle treatment make it possible to proceed to a search for monoton-
ically zoning indices common for the three objects of study without
fearing that this condition may distort the true zoning of the min-
eralization. Viewed in more general terms, a search for monotonic zon-
ing indices for standard deposits is validated by the fact that these lat-
ter have been well studied. Coupled to the treatment of the field data
of a detailed geochemical survey according to the zero cycle of the
Nu-2 program, this prevents a blind orebody from being omitted
at a deep horizon.

The purpose of the following three handling cycles is to consider
in turn all first- to third-order geochemical indices and print mono-
tonic ones concurrently for all the targets of study that are of in-
terest to us. Figure 67 presents fragments of listings for a study of
the zoning of the "Yuzhnoe" deposit from four operations of the
first cycle. In the particular case, although there was no need in
that, conventionally monotonic indices with a disturbance of the
monotony at one of the horizons as is the case of the Ag/Zn index
for the Pologaya vein were printed. This was done for educational
purposes. According to Table 16, eight chemical elements produce
28 first-order indices 24 of which proved to be monotonic and conven-
tionally monotonic for three targets of study which strongly suggests
the high degree of geochemical order of the ore veins. Referred to
individual targets, 10 indices turned out to be absolutely monotonic
for the "Glavnaya" vein, 18 for the "Tuken" vein and 7 for the "Po-
logaya" vein. Yet only three first-order indices, i.e. the Au/Co, Au/Zn
and Au/Cu ratios have proven common for the three veins.

Apart from the numerical values of monotonic and conventionally
monotonic indices the amounts of their differences between the
horizons with respect to v_{min} are printed and their graphs plotted.
In like manner second-order indices were analysed without conven-
tionally monotonic and omitting v_z graphs. As a result, of 406 in-
dices considered, 32 second-order indices proved monotonic for the
three veins from which to select the necessary number of indices

for eventual use in prospecting. The analysis of the zoning of the
"Yuzhnoe" deposit was completed at 13.59, i.e. it took some 2 min 7 s
of machine time, as is shown by the terminating listing "start" and
"stop" (see Fig. 67). In the particular case the third cycle was not
resorted to.

The vast opportunities that have opened up for determining
zoning indices following a consideration of the numerous second-,
third- and senior-order element ratios have given rise to the ques-
tion of nonrandomness criteria of the results obtained. As initial data
for handling by the use of the Nu-2 program it is possible to insert
a series of random variables imitating the results of a horizon-by-
horizon geochemical sampling. Despite the geological absurdity of
these data, it will be possible to establish with a definite degree of
probability various order indices varying monotonically throughout
the levels of a fictitious mineralized zone from among the consider-
ed ratios between these variables.

Clearly, any set of f ratios between the random variables v_1,
v_2, $v_3 \ldots v_f$ may be arranged in a decreasing or increasing
order. From among the remaining variants that are disordered only
these two sequences will be monotonic. The probability of a random
event which is the appearance of a monotonic sequence for f in-
dependent variables is governed by the ratio of the favourable out-
comes (two) to the total number of possible substitutions $(f!)$, or

$$\Pi = 2/f! \qquad (101)$$

where $f!$ is the factorial of the number f, in our case the number of
the tested horizons.

When looking for zoning sequences, a constraint is placed on
these of concurrent monotony for objects in the composition. Another
constraint placed on monotonic indices $(m\text{-}1)$ of targets of search
consists in their similar to the first target decreasing or increasing
form which twice reduces the probability of their appearance. For
independent random variables the probability of a complicated
event is governed by a product of particular probabilities:

$$\Pi_{comp} = \frac{2}{f_1!} \times \frac{1}{f_2!} \times \frac{1}{f_3!} \times \ldots \frac{1}{f_m!} \qquad (102)$$

A similar more complex relationship determines the probability
in the case of "objects n, min m", where $n > m$.

Equation (102) permits the assessment of the number of the ex-
pected randomly monotonic sequences N_{rdm} within the selected
composition Π_{comp} if N independent indices are simultaneously
considered:

$$N_{rdm} = N\Pi_{comp} \qquad (103)$$

The occurrence of a random event may differ from the mathemat-
ical expectation, remaining within definite boundaries at a specified

probability. Accordingly, Yu.V. Shvarov has calculated a nomogram for the estimation, from the value of $N\Pi$, of the number of N_{cr} which are random monotonic indices ν expected at a 95% confidence limit, given the independent character of the inserted data (Fig. 68).

To return to the results of the study of the zoning of the "Yuzhnoe" deposit, by virtue of Eq. (102) we have

$$\Pi_{comp} = \frac{2}{4! \times 3! \times 4!} = \frac{1}{1728}$$

or, for second-order indices, according to Table 19 and Eq. (103):

$$N\Pi = \frac{406}{1728} = 0.235$$

whence, by referring to the nomogram, we find that $N_{cr} = 1$. Thirty two monotonic indices have been actually determined which points to their nonrandomness.

The considered relationships (101)-(103) permit the formulation of criteria of the adequacy of the study of the reference deposit

FIG. 68. Nomogram for estimation of the critical number of randomly monotonous indices (95% confidence limit). After Yu.V. Shvarov

zoning. To be able confidently to select the necessary number of geochemical zoning indices ν the number of the established general monotonically varying ratios between the elements should be certain in excess of the number of possible random ones. It is desirable that N_{cr}—the expected number of random values of ν—should not be more than 2-3, since for $N_{cr} \geqslant 10$, whatever the number of established indices, the confidence of their selection for eventual application is impaired. If the number of the determined ν equals N during the study of a particular deposit this does not mean that the found monotonic ratios between the elements are random ones. This only suggests that we may expect that number of monotonically varying indices in conformity to principles of combinatorial analysis, given random, geologically absurd input data.

The selected zoning indices in the mineralized zone metric 0.0-1.0 should possess a sufficiently large span of R equal to ν_{max}/ν_{min} and vary fairly uniformly over this interval. The selected ν should correspond to the determined zoning sequence of element deposition in terms of the composition of the chemical elements in the numerator and denominator and should differ as much as possible in terms of the set of the elements. Generally the selection of zoning

indices is restricted to a consideration of second-order indices (zero, I and II cycles). Should the results obtained prove insufficient, the study of zoning of a standard deposit should be continued by analysing third-order indices or referring to additional geochemical field data. If the study makes use of the Nu-2 program, one should abstain from excessively complex compositions since even for $N\Pi \leqslant$ $\leqslant 0.051$ random monotonic indices cannot be expected ($N_{cr} = 0$).

In case the value of $N\Pi$ continues to decrease, zoning indices of interest to us may fail to reveal themselves as a result of natural and man-made noise.

Objects entering a composition may include orebodies of the same deposit, its various prospecting profiles or a few genetically similar deposits.

Natural geological processes are of a stochastically determined nature, that is why the empirical data deviate from straightforward functional dependences. An abstract model of an endogenic mineralization, free from natural and man-made noise, would enable us to find out its principal regularities and conduct their detailed analysis. By placing on an idealized model predetermined constraints, by referring to random noise and complications imitating the actual geological conditions, we would be able to estimate their role and ensure more adequate interpretation of the geochemical field data.
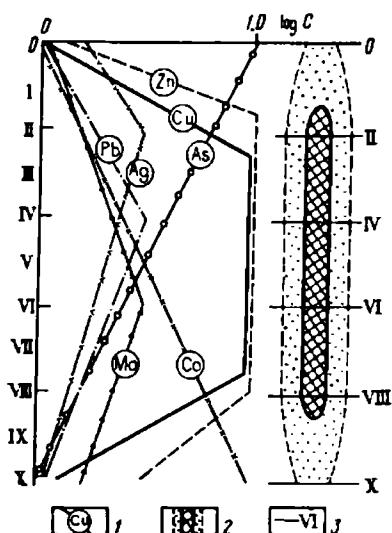
FIG. 69. Model of endogenic mineralization (vertical section):

1 — ore element content graphs; *2* — orebody and its primary halo; *3*–0 — X-horizons of mineralized zone

The model in question characterizes a vertical orebody enclosed in a primary halo bounded by the upper and lower pinchings-out and formed by a one-stage process (Fig. 69). The contents of seven ore elements are given minus background within the limits of one logarithmical interval although their absolute contents are different. In conformity with Eq. (90), by using a semilogarithmic scale of plotting, this permitted the characterization of the variations with depth of the ore element average contents in each horizon (log C_z) by means of straight lines that only differ in the angle of gradient and position of the break points. Two ore elements, Zn and Cu, are considered as the principal useful components that have been de-

posited in the orebody in a saturation regime, the remaining elements being regarded as pathfinder elements. In the upper and lower pinchings-out of the orebody the Zn content exceeds that of Cu, the As content is continuously diminishing and the Co content increasing with depth. The given model of mineralization corresponds to the zoning sequence of element deposition (reckoned from bottom upward): Co, Mo, Zn, Cu, Pb, Ag, As. In terms of geochemical characteristics the model sums up the experience collected during the studies of copper pyrite deposits in the South Urals and Mugojary.

To analyse the model by using the Nu-2 program 11 horizons have been selected spaced at intervals of 0.1 of a conventional scale. Of these the first two refer to the supraore halo (0-I), seven horizons (II-VIII) to the orebody, and the lower two (IX-X) to the subore halo. Following analysis of the initial model the determined zoning sequence of element deposition, referred to the centres of gravity of their paired ratios corresponds to the true one. The number of the established monotonically varying zoning indices includes: 5 (out of possible 21) first-order, 29 (from among 231) second-order and 153 (from among 1281) third-order indices. No monotonic indices were expected in conformity with Eq. (109).

Random interference values $\varepsilon = 1.1^{\pm t}$ and $1.3^{\pm t}$ obeying lognormal distribution with a zero mathematical expectation were imposed on the model horizon-by-horizon element contents; the model was analysed for different numbers of tested levels, at different intervals and with a fewer number of elements. The generalized evidence has enabled us to conclude that the true zoning sequence rows of element deposition can be determined provided only that the entire interval of an ore zone is studied, from the upper (0) to the lowest (X) horizons of the model. Under this condition, without taking into consideration random interference, given 11, 9, 7, 6, 5 or even 4 tested horizons, the determined sequence of element deposition is in agreement with the true sequence or inappreciably differs from this (inversions not exceeding three in number). Marked departures from the true sequences appeared when input data corresponded to minor intervals of the model analysed. So, if the upper (horizons 0-IV) and lower (horizons VI-X) intervals of the model are analysed, the determined sequences of element deposition significantly differ from the specified ones. Unless supraore, central and subore horizons are tested, we are likely to establish zoning sequences which are far from being true ones.

The negative effect of random noise factors on the handled results is evident, hence the need to decrease their amplitude by a better quality of geochemical sampling, analysis and calculations. Senior-order indices are less liable to the effect of random noise and are more likely to be monotonic. Figure 70 illustrates the de-

rivation of a monotonic third-order index $\nu = \dfrac{As \cdot Ag^2}{Pb \cdot Mo \cdot Co}$ from three first-order indices complicated by a random noise $1.3^{\pm t}$. Constant interference factors equally affecting the contents of all ore elements (pinches and swells, screening effects etc.) do not influence dimensionless zoning indices.

Separate analysis of zoning of solely the upper interval (horizons 0, I, II, IV), solely the intermediate (horizons III, V, VI, VIII)
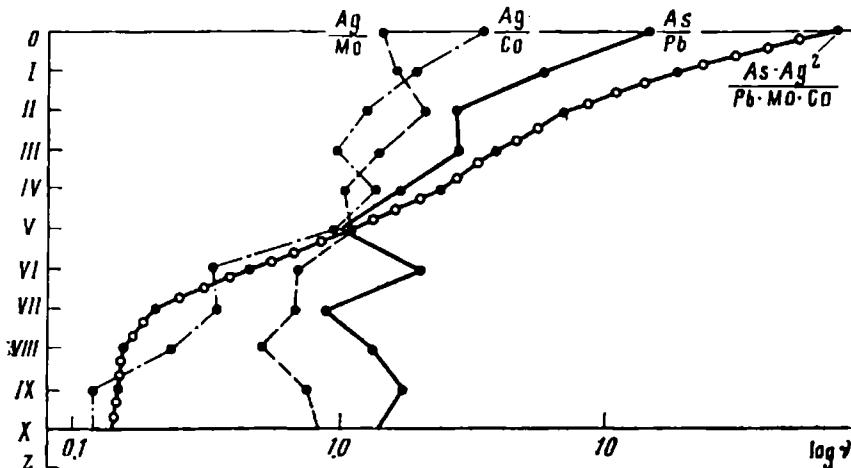
FIG. 70. Graphs of 3rd order monotonic index formed from 1st order non-monotonic indices. After E.I. Babaev

and solely the lower (horizons VII, IX, X) yielded unsatisfactory results. Despite the fact that numerous monotonically varying first- and second-order ratios (125 to 219) have been determined, their contradictory form and a large number of possibly random variables (over 30 at the top and middle and over 100 at the bottom) rendered the choice of zoning indices practically not feasible. A negative ranking correlation $r = (-0.54)$ was revealed between sequence rows of zoning of element deposition for the upper and the lower intervals of the model. Under conditions of a really existing deposit this might lead one to an erroneous assumption as to the presence of a reverse zoning of the mineralization.

On the other hand, when limited ore zone intervals are tested in individual prospecting profiles or orebodies the advantages of the Nu-2 program can be distinctly seen. By combining three intervals of the model under study to form one composition (Fig. 71) according to the scheme "targets 3 (min 3)", we find 5 first-order common monotonic indices and 29 second-order ones with one possibly ran-

dom variable and a general sequence of zoning of element deposition which is in full agreement with the previously obtained results when all 11 horizons of the initial model were analysed. On the whole, this and other model studies have pointed to the high efficiency and reliability of determinations of zoning of deposits through the use of the Nu-2 program.

Figures 72 to 74 present geological sections of a mercury, a stratiform polymetallic and tin ore deposits and zoning indices of these deposits found by handling the field data using a 062-MGU (Moscow State University) program whose improved version is the Nu-2 program. Referred to the number of the tested prospecting profiles and mineralization levels, the determined indices were not expected to contain random monotonic ones. 8-10 different values of v were selected for each of these thoroughly investigated deposits to be then used to estimate genetically similar ore showings— geochemical anomalies to be located in prospecting work.

The zoning of the Terligkhai deposit (see Fig. 72) was studied as a whole, without isolating separate quartz cinnabar orebodies

FIG. 71. Determination of total zoning sequence of deposit from data on testing different intervals of mineralization ("Nu-2" program). After E.I. Babaev.

Mineralized zone intervals: a — upper; b — middle; c — lower; 1 — orebody and its primary halo; 2 — horizons being tested

which proved to be correct. Genesis of stratiform deposits is considered dubious. Some believe they are of a primary sedimentary character, others consider them to be of hydrothermal origin. The geochemical zoning of the Mirgalimsai multicomponent metal deposit equally well reveals itself in the two anticlinal limbs (see Fig. 73) which suggests a possible postorogenic character of the mineralization and, consequently, its epigenesis. Two tin ore deposits shown in Fig. 74 are of the same genetic type of a silicate sulphide formation, the shortest distance between them being some 40 km. The similarity coefficient x of the two deposits is about 1.0.

Are we always to expect monotonic zoning indices if there was sequential element deposition during the formation of ore? Certainly not. One of the causes of the disturbance of their monotony is a many-storied, sometimes echelon-like location of orebodies. Therefore zoning sequences may be repeated many times, and as a result, the

FIG. 72. Graphs of geochemical zonal indices and geological section of a Ter-ligkhai mercury deposit. After G.S. Simkin:

1-3 — Low Devonian volcanites: *1* — andesite and dacite porphyrites; *2* — tuff-breccias; *3* — aphyric andesite porphyrites; *4* — main and secondary faults; *5* — orebodies and their primary halo in a contour $3 \cdot 10^{-3}$ % Hg; *6* — underground pits (*a*) and boreholes (*b*)

$$\nu = \frac{Ag \cdot Hg^2}{Pb \cdot Zn^2}$$
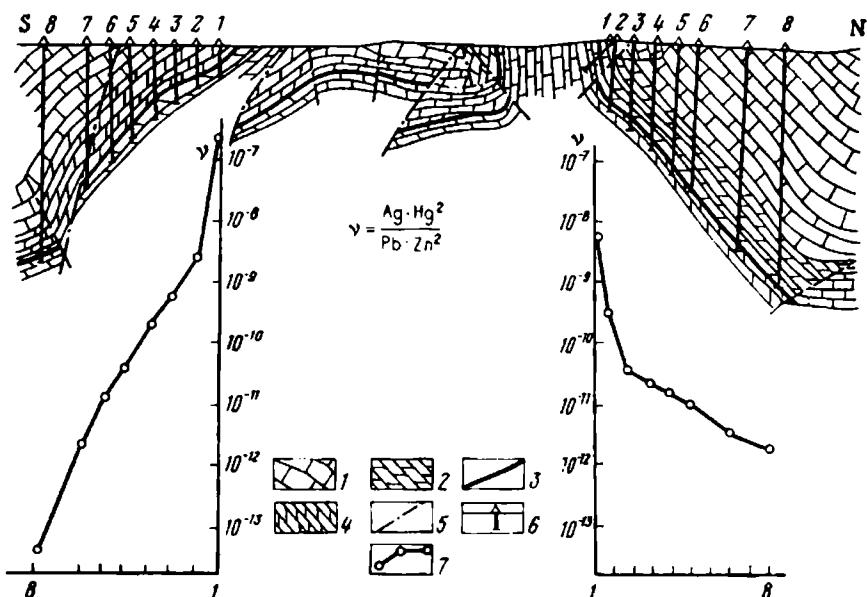
FIG. 73. Graphs of alteration of geochemical zoning index with depth. Mir-galimsai deposit:

1 — limestones $C_1 t_1$; *2* — limestones $D_3 fm_{5-8}$; *3* — ore horizon $D_3 fm_4$; *4* — limestones $D_3 fm_{1-3}$; *5* — tectonic disturbances; *6* — exploratory boreholes; *7* — $\nu_z = f(z)$ graph

subore aureole of one orebody may pass to the supraore aureole of another orebody. This important feature must invariably be taken into consideration.

Another reason may be a centriclinal zoning symmetrical about the middle part of an ore deposit. Such zoning may be expected for volcanic sedimentary deposits and along the strike (v_y) of many
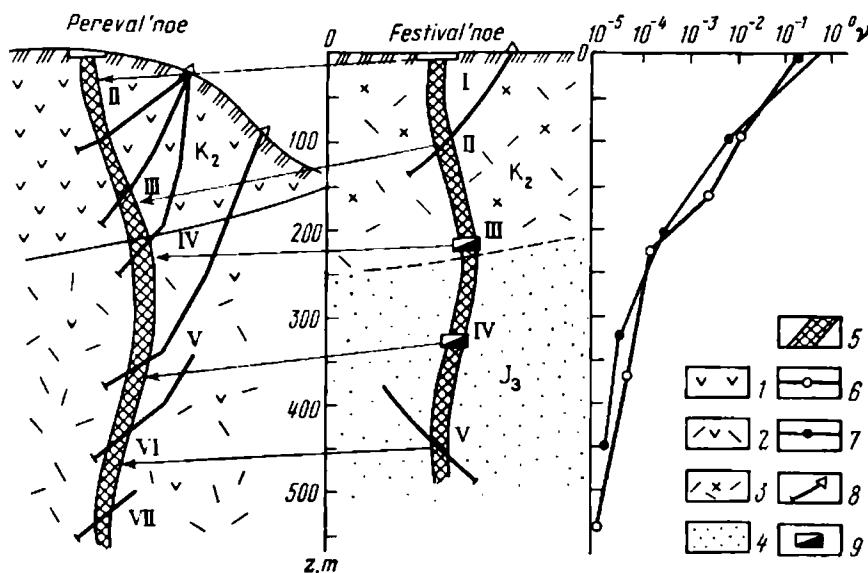
FIG. 74. Geological sections of two tin ore deposits and graphs of common to hem geochemical zoning index $|v_z = (\frac{Bi^2 \cdot Ag}{Sn^2 \cdot W} : |||$

1 — porphyrites; 2 — plagioclase porphyrites and their tuffs; 3 — effusive and sedimentary rocks of the Lower Cretaceous; 4 — Upper Jurassic sandy slate rock mass; 5 — mineralized zone; 6, 7 — graphs of v_z for deposits Pereval'noe (6) and Festival'noe (7); 8 — boreholes; 9 — mine workings

vein and seam-like endogenic deposits from the "hot" central portion to "cold" wings. A distinct centriclinal zoning has been discovered by A. A. Matveyev for a copper pyrite deposit "Fiftieth Anniversary of October" (the North Mugojars).

A similar role is played by gently sloping orebodies as a result of which certain prospecting profiles disclose no zoning or one of a reverse character (Fig. 75). This type of zoning has been discovered during an investigation of the Koksai, South Kazakhstan, porphyry copper deposit. Isolines of conventional "temperature" of ore deposition mirrored by lines of iso-v in the plane of the mineralized zone may be assumed parallel to the ground surface and to one another only in the first approximation. The term "temperature" is deliberate-

ly put! in inverted commas and means a complex of physicochem-
ical conditions changing with depth. The second approximation
may be provided by an "isotherm" pattern shown in Fig. 75. In a
more general case lines of iso-v in the plane of the mineralized zone
are of a complex curvilinear character closing on themselves about
individual "colder" and "hotter" blocks.
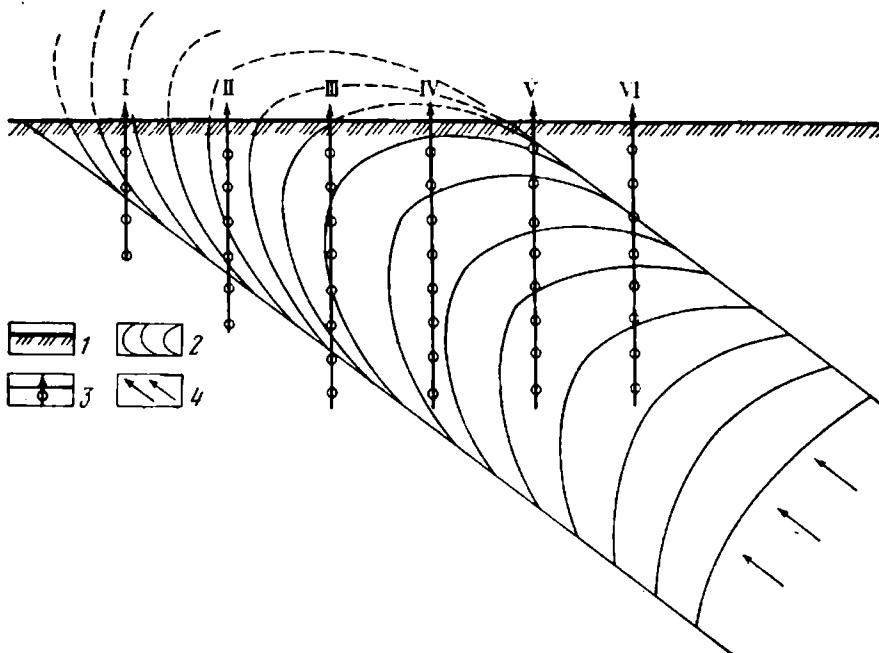
FIG. 75. Diagram showing inverse zoning for mildly dipping mineralized zone:
1— modern surface; 2 — conventional "isotherms" of ore deposition; 3 — prospecting pro-
files, points indicate intersection of mineralized zone plane by boreholes; 4 — direction
of movement of hydrotherms

To disclose an association between the distribution of the useful
components of a mineralization and numerical values of v are of
much practical importance, in particular, for the prognostication
of ore shoots and bonanzas in gold deposits. To be sure, various fac-
tors, including a multistage character of the mineralization, act
to complicate the zoning of endogenic deposits under natural con-
ditions.

Sec. 4.4. Prospecting and Assessment of Deposits

It is the ultimate purpose of studies of the primary halos and the
zoning of deposits to pinpoint new orebodies and prognosticate the
depth of mineralizations. These tasks have been effectively solved

by S.V. Grigoryan in the mountainous regions of Karamazar, Tajik SSR. Of 37 geochemical anomalies he proposed for exploration 31 concealed orebodies (84%) have been located by prospecting bore-holes. Of 15 anomalies estimated to be of no importance none has proven to contain economic ore. Blind orebodies have been discovered following a prognostication by S. V. Grigoryan at deep horizons of the Harpenberg skarn polymetallic metal deposit, Sweden [3].

Irrespective of the exploration and prospecting stage, the evaluation of individual ore intersections from geochemical field data by converting these into the metric of a known standard deposit is of crucial importance. This is particularly so, dealing with a mineralization of no economic value, when one has to determine whether it refers to the supraore, barren central or subore interval of a mineralized zone (see Fig. 55).

Of no lesser importance, too, it is to assess in terms of the metric of a known standard deposit an economic mineralization at a horizon where it has been pinpointed by exploratory boreholes or the modern ground surface from a secondary residual dispersion aureole as well. In the latter case we have to determine, apart from other characteristics of expected reserves of the deposit, the horizon of its erosion cut off (cf. Sec. 6.2.4).

The taxation of the mineralization horizon is carried out from zoning indices v_z of a genetically similar standard deposit. To do this, the selected monotonically changing zoning indices are plotted in a [log v, z] coordinate system as shown in Figs. 64, 72-74. These graphs, used much as graduation scales, enable the numerical values of v_i of the cross section of interest to us to be converted to the values of z_i. It is best to express standard z values in terms of a scale 0.0 to 1.0. If sufficient data are not available, the depth is measured in relative or absolute elevations or in horizons of a standard deposit. The same estimates may be obtained analytically from similar triangles:

$$z_i = a + (b - a) \frac{\log(v_a/v_i)}{\log(v_a/v_b)} \qquad (104)$$

where a and b are elevations (or sequence numbers) of the two horizons of the standard deposit between (or near) which z_i is located (Fig. 76).

It is not sufficient to determine the horizon of a mineralization from one value of v, since the convergence and confidence limits of estimates remain unknown. A better plan is to make determinations from 8 to 10 different values of v followed by the estimation of the arithmetical mean of z and standard deviation through the spread of values, $s = \beta_n (z_{max} - z_{min})$ where β_n is a tabular coefficient governed by the number of determinations [34]. Estimates of mineralization horizons are represented in terms of $z \pm s/\sqrt{n}$, where n

is the number of v used. The values of the confidence limits $\pm s/\sqrt{n}$ characterize the reliability of the estimates and provide a criterion of the genetic affinity of the deposit being assessed to the standard deposit. Estimates are considered satisfactory if they are within ± 50 m. If the confidence limits are larger, it is better to choose a different standard.

The method for the evaluation of metal reserves at deeper horizons by referring to the supraore primary halo parameters has first been suggested by V.L. Barsukov for tin ore deposits of the Soviet Far East. Basically, it consists in analyses of the primary halos of readily volatile elements liberated in the course of the decomposition of complex compounds involved in the transport of ore elements during hydrothermal ore deposition. In the general case there is a direct relationship between the supraore halos associated with these indicator elements and the amount of metal deposited at deeper levels. As ore tin deposits are being formed, the transport of tin by hydrothermal solutions is made possible by fluorine hydroxide complexes hydrolysis of which, on a change in redox conditions, occurs as follows:
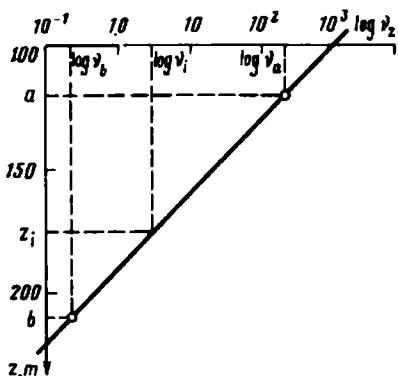
FIG. 76. Plot for estimation of mineralization horizon z_i from value of v_i in terms of metric of standard deposit

$$[Sn(OH)_2F_4]^{2-} + 2OH^- \rightarrow SnO_2 + 2H_2O + 4F^-$$
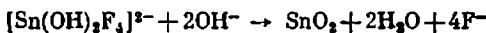
The fluorine ion released in this process is a component of the supraore adjacent rocks whose content is governed by the amount of cassiterite deposited at depth [3].

V.L. Barsukov has proposed to evaluate prospective tin reserves from the ratio between the average contents of fluorine in the supraore interval of an ore vein (F_p) and in the adjacent aureole (F_{op}) through the use of a respective regression equation. These relationships have been used with a different degree of success in practical work and have been incorporated in the acting Manual [17]. This most promising method of evaluation of prospective reserves of Sn as well as of W, Be and some other metals by referring to the primary supraore halos associated with volatile elements needs further improvement.

Another version of solving this problem is valid for a more limited interval of supraore halos, i.e. from a horizon where the principal useful component is found in obviously anomalous amounts to a hori-

zon of economic ore. In terms of the accepted metric this corresponds to the interval $0.0 < z < 0.2$. Given $z \geqslant 0.2$, the reserves are evaluated by referring to the parameters of the orebody. The supraore primary halo, say, associated with a lead deposit may be characterized by successive horizons shown diagrammatically in Fig. 77.
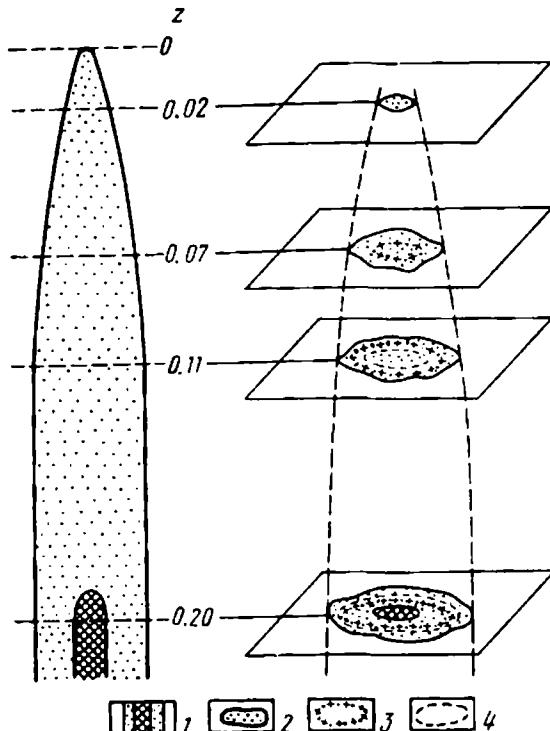
FIG. 77. Model of levels of erosional surface:
1 — vertical section across orebody and its primary halo; primary halos in plan; *2* — Pb; *3* — Ag; *4* — Cu

It is only Pb that gives rise to a lithochemical anomaly of minor size and productivity at the horizon 0.02. At the 0.07 horizon silver follows, at the 0.11 horizon copper, and the discovered dimensions of the anomalies increase successively. If the primary Pb halo appears earlier than the Ag halo this does not mean that silver was deposited below lead, and it is impermissible to judge of the behaviour of the elements from the established dimensions of their geochemical anomalies. This sequence in the origination of the halos associated with the two elements is ascribed to the fact that we deal with a lead deposit and in quantitative terms Pb is essentially predominant with respect to Ag.
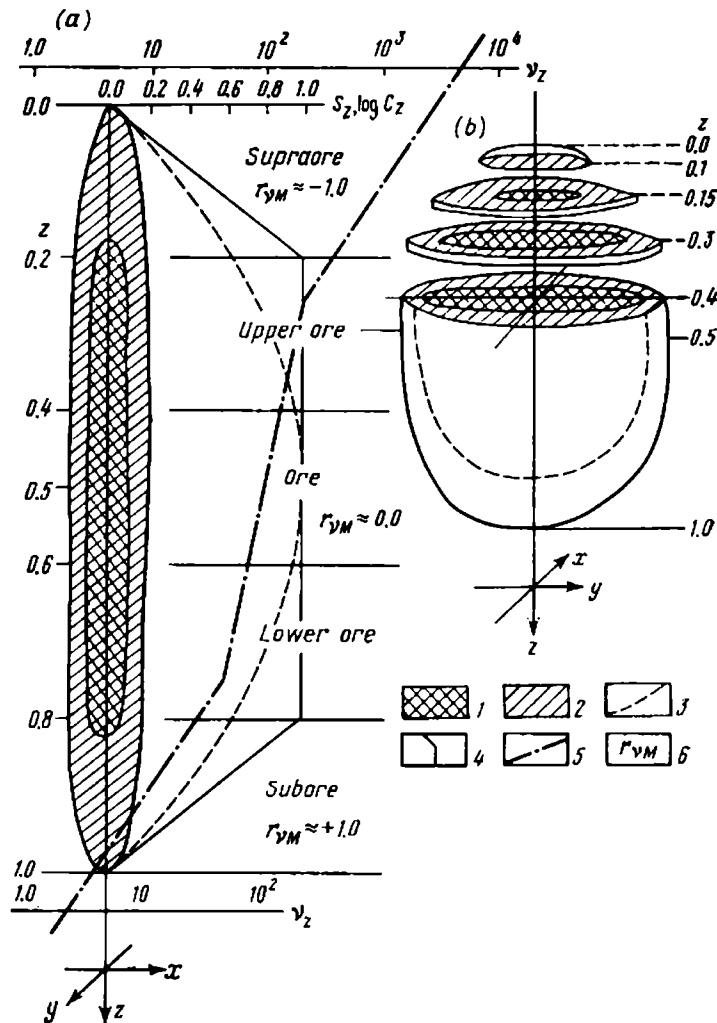
FIG. 78. Model of ore lens:

a — vertical section; *b* — different levels of erosional surface. *1* — orebody; *2* — primary halo; *3* — graph of area of lithochemical anomaly S_z; *4* — graph of ore element content $\log \overline{C}$; *5* — graph of v_z; *6* — coefficients of correlation between v_z and M_z at different mineralized zone intervals

   This straightforward model only serves to remind us that the effective dimensions of lithochemical anomalies, element contents and productivities even in the supraore halo may vary in a multitude of ways, increasing, remaining constant or diminishing with depth. Figure 78 shows in more detail the principles of distribution of the principal ore constituent in the contour of the mineralization model. Here the vertical cross section of an ore lens shows: the aforementioned graph of the ore element contents of $\log C_z = f(z)$, a graph of the change with depth of the area of the lithochemical anomaly S_z and a graph of one of geochemical zoning indices v_z which, according to the conditions, does not include the principal ore element.

   By jointly considering these data it is possible to identify within the mineralized zone the following intervals: the supraore where the linear, M_p, and the areal, P_p, productivities of the mineralization increase from horizon to horizon; the ore ones, where M_p remains relatively constant; and the subore one where the productivity diminishes until the mineralization completely thins out. The value of the zoning index v_z monotonically dropping with depth, there is a negative correlation between M_p and v_z in the supraore interval and a positive correlation in the subore interval, and there is no correlation in the most productive portion of the mineralized zone. During geochemical testing of a particular deposit on a series of prospecting cross sections these correlations may be used for the prognostication of the mineralized zone intervals of interest to us.

   The right-hand part of Fig. 78 presents different ore lens surfaces starting from the supraore horizons 0.1-0.15. Clearly, geochemical exploration may permit a concealed orebody to be discovered also at other, higher, horizons of a primary aureole with different negligible productivities P_p (in m² %). It is possible to evaluate the prospective metal reserves at deeper horizons from the magnitude of this productivity through the use of Eq. (87) only if we refer it to the horizon 0.2 by introducing a correction coefficient known to be greater than unity.

   The prospective metal reserves Q_H^* in concealed orebodies should be evaluated from the productivity P_p of supraore halos associated with them by using these relationships:

$$P_p^* = \eta P_p \tag{105}$$

$$Q_H^* = \frac{1}{40} P_p^* H \alpha \tag{106}$$

where P_p^* is the corrected productivity; $\eta_i = f(z_i) > 1.0$ (z_i is the particular horizon of the supraore halo at which P_p is determined); H is the extent of the ore interval from $z = 0.2$ to $z = 0.8$; $\alpha < 1.0$ is a correction coefficient taking into account the fraction of poor grade ores. Unlike the coefficient $\eta > 1.0$ governed by $z < 0.2$, the correction coefficient α in Eq. (106) depends, in particular, on

the total metal reserves Q_H concentrated in the given target of assessment.

It is shown by experience that the established width of the primary halo, given constant least economic and background contents, is governed by the properties of the ore element and enclosing rocks and is independent of the size of the orebody. Eventually, as the total metal reserves Q_H increase, the relative metal percentage located in the primary halo decreases, and the correction coefficient α tends to unity. The fact that α does depend on Q_H can be shown by a simple model of a spherical deposit. If we denote the radius of an orebody by r, the average metal content in the ore by $\bar{C}_p$, and if we assume the equivalent thickness of the primary halo to be 1.0 and the average metal content to be $0.2\ C_p$, then we have

$$\alpha = \frac{r^3}{0.8r^3 + 0.2\,(r+1)^3}$$

By assigning different values to r, we can find the corresponding values of α (Table 17). With increasing the size of a deposit the metal

TABLE 17

Correction Factors α to Allow for Low Grade Ores. Spherical Deposit (a Model)

Target of study	r	Conventional metal reserves			α
		Total Q_H	including:		
			ore	primary halo	
Ore showing	0.3	0.461	(0.027)	0.434	0.059
Deposit:					
small	1.0	2.4	1.0	1.4	0.417
medium	2.15	14.26	10.0	4.26	0.701
large	4.64	115.88	100.0	15.88	0.863
unique	10.0	1067.4	1000.0	67.4	0.937

reserves in the primary halo are enhanced, but their relative fraction in the total (geochemical) reserves diminishes.

To account for the numerical values of the coefficient $\eta_i > 1.0$ is more difficult. The functional relationships of interest to us still have to be established. At this point, we will restrict ourselves to considering the particular values of η_i proposed for the calculation of the productivities of the supraore primary halos in terms of the economic ore horizons ($z = 0.2$) for tin ore deposits of the Kavalerovsky district (Maritime Region).

Tin ore deposits of this district refer to a sulphide cassiterite formation, their orebodies appear as steeply dipping veins and mineral-

ized fractured zones. The mineralization features a distinct vertical zoning which is mirrored by monotonically decreasing with depth geochemical zoning indices such as $\dfrac{Pb}{Sn}$, $\dfrac{As \cdot Zn}{Sn^2}$, $\dfrac{Sb \cdot Cu \cdot Pb}{Sn^3}$ common for the principal deposits in the district. Figure 79, a, b, and c shows a
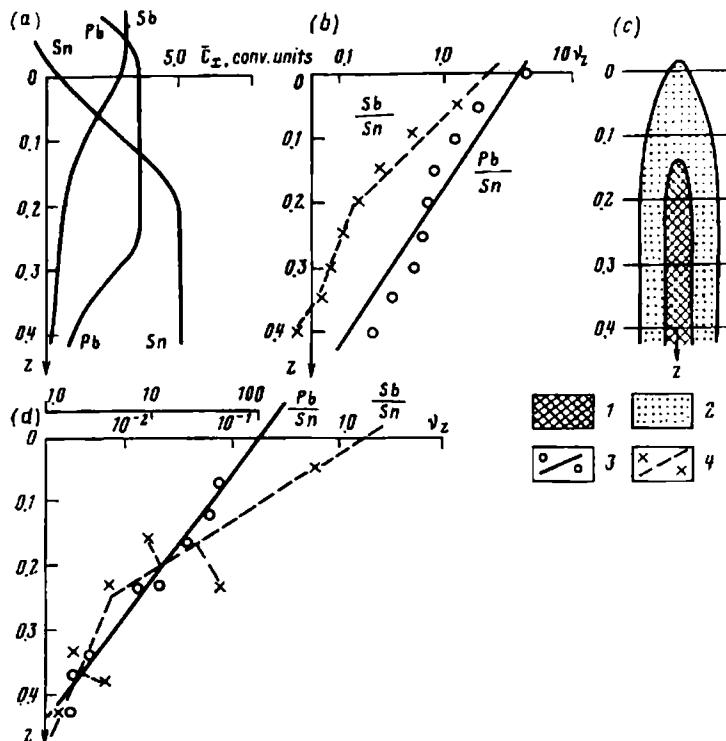
FIG. 79. Graph of Sn, Pb, Sb contents and ratios between them in supraore and upper ore intervals of tin deposits. After A.P. Solovov and P.A. Kurshev: a, b, c — model; d — actual data on Kavalerovsky ore district. 1 — orebody; 2 — primary halo; 3-4 — calculated values and Pb/Sn (3) and Sb/Sn (4) graphs

model of the upper interval of a mineralized zone with theoretical graphs of the average content C_z of three elements, Sn, Pb, Sb, and ratios between them, v_z. By contrast to the increasing Sn content, average Pb content manifests stable values throughout the supraore interval, the Sb content continuously dropping with depth in the same interval of $0.0 \leqslant z \leqslant 0.2$. The fact that the value of the first-order geochemical index $v = $ Pb/Sn diminishes with depth in the supraore interval is only governed by an increase in the average Sn content (productivity) and, consequently, is a measure of a correc-

tion coefficient η. The continuing decrease of the numerical values of $\nu = $ Pb/Sn below the elevation $z = 0.2$ under conditions of the stable Sn content is due to the decrease with depth of the average Pb content. The more rapid drop with depth of the ratio Sb/Sn in the supraore interval results from the joint effect of the increasing Sn average content and decreasing Sb content and cannot provide a measure of the correction coefficient η.

Figure 79 presents the actual graphs of variation with depth of the numerical values of the Pb/Sn and Sb/Sn ratios for the Kavalerovsky ore district that fairly closely approximate model conditions (see Fig. 79c). By this token, the actual graph $\nu = $ Pb/Sn, in conformity to the relationship $\eta = $ $= \nu_{z<0.2}/\nu_{z=0.2}$, was used to find the values of $\bar{\eta} = f(\bar{z})$, a graph of which is shown in Fig. 80. If the erosion surface level is close to zero, the values of η increase at such a rate as to render their estimation unreliable. That is why the use of a correction coefficient and evaluation of prospective metal reserves from Eqs. (105) and (106) if the erosion surface level is $\bar{z} < 0.02$ is warned against, for $z \geqslant 0.2$ the coefficient η is unity.
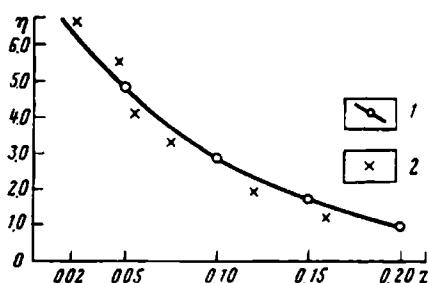
FIG. 80. Plot for estimation of correction coefficient $\eta > 1.0$ for small depth of erosional surface of tin ore showings of Kavalerovsky ore district. After A. P. Solovov and P. A. Kurshev:

1 — principal graph of $\eta = f(z)$; 2 — relative linear productivities M_z along strike of Arsen'evskii deposit for six values of z from 0.02 to 0.16

In addition, Fig. 80 shows the values of η calculated from linear productivities, M, of Sn secondary halos associated with the Arsenievsk deposit for six different values of z. When dealing with deposits of other genesis and different metals, alternative combinations of ore elements for finding η by the above method are possible.

We can estimate metal reserves to be expected below the level $\bar{z} > 0.2$ by allowing for the remaining proportion of the ore deposit H through this straightforward relationship:

$$H_i : H_{tot} = (0.8 - \bar{z_i}) : (0.8 - 0.2) \quad \text{or}$$

$$H_i = H_{tot} \frac{0.8 - \bar{z}}{0.6} \qquad (107)$$

The term z can represent here the erosion surface level of the mineralization or depth reached by prospecting boreholes below which mineralization reserves are estimated from the geochemical field data referred to this horizon. At $z_i \geqslant 0.8$ the expected reserves are zero. The total extent of the ore interval H_{tot} is empirically deter-

mined or by constructing models based on the geometrical similarity of genetically similar deposits of different size groups. The mineralization model should be decided on by referring to the closest mode and elements of occurrence of the expected orebody.

It is possible to substantiate a relative evaluation of genetically similar deposits following from their geometrical similarity. Such is the case of two porphyry copper deposits in the North Balkhash region. The first of these, is the well-known Kounrad, the other is the Sokurkoi deposit discovered shortly later in the vicinity of the former. Exploratory efforts undertaken during the last five decades have yielded no results. A study of the primary zoning of the two deposits carried out during the recent years has disclosed their total geochemical affinity. Zoning sequences of 12 ore elements of the Kounrad and Sokurkoi have a ranking coefficient of correlation 0.65 (for r_s % = = 0.58). The two deposits manifest a number of common zoning indices v monotonically changing with depth. Graphs of the same

FIG. 81. Plots for estimation of coefficient of similarity between two copper porphyry deposits. After A.A. Matveev:
1 — Kounrad deposit; 2 — Sokurkoi deposit

zoning indices for the Kounrad and Sokurkoi show essentially different inclination to the abscissa axis which can be seen from Fig. 81. By referring to the relations of the tangent angles of inclination in the graphs of seven common zoning indices using Eq. (95) it was possible to estimate a coefficient of geometrical similarity between the Sokurkoi and Kounrad deposits equal to $x = 0.27 \times 1.07^{\pm1}$. Hence, by virtue of Eq. (97), the total metal reserves of the Sokurkoi, Q_S, and the Kounrad, Q_K, are thus related: $Q_S = x^3 \times Q_K =$ = $0.02Q_K$. Prospecting of the Sokurkoi deposit seems to be unlikely to yield any promising results. Ore lodes of porphyry copper deposits often appear as an overturned vial with a barren nucleus. In the particular case the estimates were made by referring to the principle of similarity without taking into account the shape of the orebodies.

Hydrochemical, Atmochemical and Biogeochemical Methods of Mineral Exploration

To decide on the particular method of geochemical exploration we have to proceed from whether it is the most efficient one under given geological and economic conditions. If two, three or even four methods can be successful, it is best to choose one, less commonly, a combination of two methods, so that the task in mind can be achieved with least efforts and costs. The close relationship between geochemical anomalies in the geospheres (see Sec. 1.7, Fig. 11) makes it possible to prognosticate similar, to a definite extent, results of geochemical surveys by different techniques. However, the fact that anomalies may be located by two or more geochemical methods cannot validate their joint use.

Geochemical methods find the largest use in exploration for solid phase mineral. Lithochemical techniques are generally employed here. According to foreign workers [27], an annual 18 million geochemical samples is being collected throughout the world of which 97.5% are lithochemical, 2%-hydrochemical and 0.5%-biogeochemical samples. The atmochemical technique is mainly used in exploration for oil and natural gas fields, the data on annual volumes of such operations are not available. The total fraction of atmochemical surveys for deposits of fossil fuels, ore mineral and non-metallic mineral resources which is much less than that of lithochemical surveys is likely to markedly increase in immediate future. As to lithochemical, hydrochemical and biogeochemical surveys that tend to slowly increase, the proportion between them seems to have been stabilized.

In accord with the role being played and promise offered by each of the geochemical methods of exploration we will briefly outline the basic principles of the hydrochemical and biogeochemical techniques, and in some detail of the atmochemical technique.

Sec. 5.1. The Hydrochemical Method

This method consists in analyses of the chemical composition of natural surface and subsurface waters. Basically, the method relies on the ability of water to dissolve rocks, the active role played by water in chemical transformations of minerals and its properties

as a mobile medium. The intimate connection between the chemical composition of water and the presence of mineral deposits in the vicinity of the water stream is obvious and is one of the factors responsible for the origination of hydrochemical anomalies that may serve as guide to ore. The capacity of water to migrate from deeper horizons to the ground surface has long attracted the prospector causing him to sample natural waters for exploratory purposes.

Deposits of mineral salts, such as all kinds of natural chlorides and sulphates are the most advantageous targets of hydrochemical surveys. The total content of these compounds in natural brines may exceed 350 g/l. These may be stable in solutions being ultimately responsible for the salt composition of oceanic water (the total salt content being 35.6 g/l). If we take into consideration the fact that the total mineral content of natural potable, including stream, waters is generally 1.0–0.5 g/l, we may easily see the wide range of anomalous salt contents in surface and subsurface waters.

In view of specific features of the origination of salt forming basins which represent large and stratigraphically uniform geological entities, geochemical methods of prospecting for mineral salt deposits failed to find universal use, although as early as the beginning of the present century N. S. Kurnakov and P. I. Preobrazhensky made attempts to predict the character of salt deposits from the chemical composition of natural waters. The hydrochemical method of prospecting for potassium salt deposits proposed by M. G. Valyashko is of indisputable practical value. The hydrochemical method may prove efficient in a search for mineral sources, notably, economic bromine waters and borate deposits. Along with other active aqueous migrants, these elements manifest increased values of the thalassophyly coefficients (Br — $\tau_x = 30$; B — $\tau_x = 0.4$).

The hydrochemical method of the search for ore deposits began to be intensively developed in the USSR early in the 1950s, following the first publications by E.A. Sergeev and O.A. Alekin. The principal contributions to this field were made by S.P. Albul, A.A. Brodsky, V.V. Polikarpochkin, P.A. Udodov, later by G.A. Goleva, S.P. Krainov, S.L. Shvartsev and many others. Hydrochemical methods of prospecting for oil and gas fields have been elaborated by V.A. Sulin, V.A. Kovda, P.S. Slavin, L.A. Gulyaeva.

Of ore deposits the most advantageous targets for hydrochemical exploration are sulphide, primarily pyrite polymetallic metal deposits and copper pyrite deposits particularly rich in disulphides. Natural waters are enriched by ore elements mainly during the supergene oxidation of sulphide ores in the course of which insoluble but unstable sulphides pass through a stage of soluble sulphates before they convert to stable and insoluble secondary minerals. This process is considered at length in Sec. 3.4, the data on mineral solubilities are presented in Table 14.

Subsurface waters that wash an oxidizing sulphide deposit give rise to hydrochemical dispersion aureoles and flows associated with ore elements and sulphate ion. The ore element contents in acid ore waters of intensely oxidizing pyrite deposits may attain unusually great values (in mg/l): 45 600 for Cu, 50 300 for Zn, 30 000 for Ni etc. Following the interaction with the subsurface waters and rock minerals, chemical exchange reactions, coprecipitation and sorption, ore elements in waters pass to a solid phase and their contents rapidly drop to equal background. The direction of this process can be inferred from the values of the average contents of the ore elements in the supergene natural waters that are in the range from $n \cdot 10^{-2}$ to $n \cdot 10^{-5}$ mg/l and, notably, from their thalassophyly coefficients (Table 18).

The values of τ_x indicate that the ore element contents in the lithosphere are greater by a factor of a few hundred or even tens of thousands compared with the hydrosphere. One of the factors responsible for these values is that hydrous oxides of most metals precipitate at the pH < 7.0, whereas natural waters commonly show a neutral or weak alkali reaction. Hardly soluble oxides, carbonates, silicates, phosphates of ore elements and other end products of oxidation of sulphide minerals display negligible values of solubility products. An important role in the passage of ore elements from a solution to a solid phase is being played by the coprecipitation with Fe and Al hydrous oxides which begin to precipitate in acid solutions: $Fe(OH)_3$ at the pH $= 2.5$, $Al(OH)_3$ at the pH $= 4.2$. Essentially important is the sorption of ore elements on organic and mineral colloids, particularly, during coagulation of silica gels, on Mn hydrous oxides and many argillaceous minerals. If the sorption of anions and cations shows a multilayer pattern, the original sign of the charge of the colloidal particle does not matter.

Notwithstanding all these processes of "selfpurification" of natural waters from ore mineral contents, the enhanced, anomalous concentrations persist in stream and subsurface waters 500 to 1 000 m, sometimes a few km away from deposits. This is inferred from a multitude of forms of the occurrence of ore elements in complex multicomponent systems that natural waters represent. Aqueous ore element migration involves simple ions, complex inorganic compounds with different ligands, in particular, in an anionic form, as well as various metallorganic compounds exhibiting marked solubility. The experience gained in hydrochemical exploration strongly suggests that it is feasible to locate ore deposits by looking for aqueous aureoles and dispersion flows. The last 30 years have been witnessing hydrochemical techniques of search conducted on different scales in the ore districts of the USSR. As a hydrochemical anomaly discovered by E.E. Kuz'min in the valley of the river Kharaelakh, Krasnoyarsk Region, was being tested, the first exploratory boreholes

TABLE 18
Hydrochemical Characteristics of Ore Elements [23]

Element	Average content in waters of supergene zone mg/l	τ_x	Onset of deposition of hydroxides		Solubility Product	Behavior in supergene zone
			Cation	pH		
Pb	2.2×10^{-3}	3×10^{-4}	Pb^{2+}	6.0	7×10^{-16}	Coprecipitation with hydroxides of Fe, Mn; formation of oxides, carbonates, phosphates; sorption
Zn	3.4×10^{-2}	6×10^{-4}	Zn^{2+}	5.2	4.5×10^{-17}	Coprecipition with hydroxides of Fe; formation of carbonates and silicates; in solution, complex compounds
Cu	5.6×10^{-3}	4×10^{-4}	Cu^{2+}	5.4	1.6×10^{-19}	Coprecipitation with hydroxides of Fe, Al; sorption; formation of hydrocarbonates and silicates
Ni	3.3×10^{-3}	5×10^{-5}	Ni^{2+}	6.7	8.7×10^{-19}	Sorption by SiO_2 gels and major element hydroxides; formation of hydrosilicates
Co	8.3×10^{-4}	5×10^{-5}	Co^{3+} Co^{2+}	— 6.8	2.5×10^{-46} 1.3×10^{-15}	Sorption by clay minerals and organic matter; coprecipitation with hydroxides of Fe, Mn
Sn	4.1×10^{-4}	1.2×10^{-3}	Sn^{4+} Sn^{2+}	2.0 3.0	1×10^{-57} 1×10^{-27}	High resistance of SnO_2
W	(1×10^{-4})	7.7×10^{-2}	W^{6+}	—	—	Hemosorption by hydroxide of Fe; coprecipitation with $CaCO_3$; formation of wolframates; in solution, complex anions
Mo	2×10^{-3}	9×10^{-4}	Mo^{4+}	—	1×10^{-50}	Sorption; coprecipitation with hydroxides of Fe and $CaCO_3$; formation of molybdite and povellite; in solution, complex compounds
Sb	1.5×10^{-3}	1×10^{-3}	Sb^{3+}	0.9	4×10^{-42}	High stability of secondary oxides of Sb; in solution, complex compounds
Hg	9.1×10^{-4}	3×10^{-4}	Hg^{2+}	7.0	3×10^{-26}	Bonding of Cl^-; sorption
Ag	2.9×10^{-1}	4.3×10^{-3}	Ag^+	9.0	2×10^{-8}	Bonding of Cl^-; native state
Au	2.7×10^{-5}	9×10^{-4}	Au^+	—	1×10^{-53}	Native state

pinpointed sulphide ores thus facilitating the discovery of a copper and nickel deposit.

The acting Manual [17] recommends the use of the hydrochemical method in covered areas in the search for deep ore deposits on 1 : : 200 000 to 1 : 25 000 scales which is clearly justified. The prin-
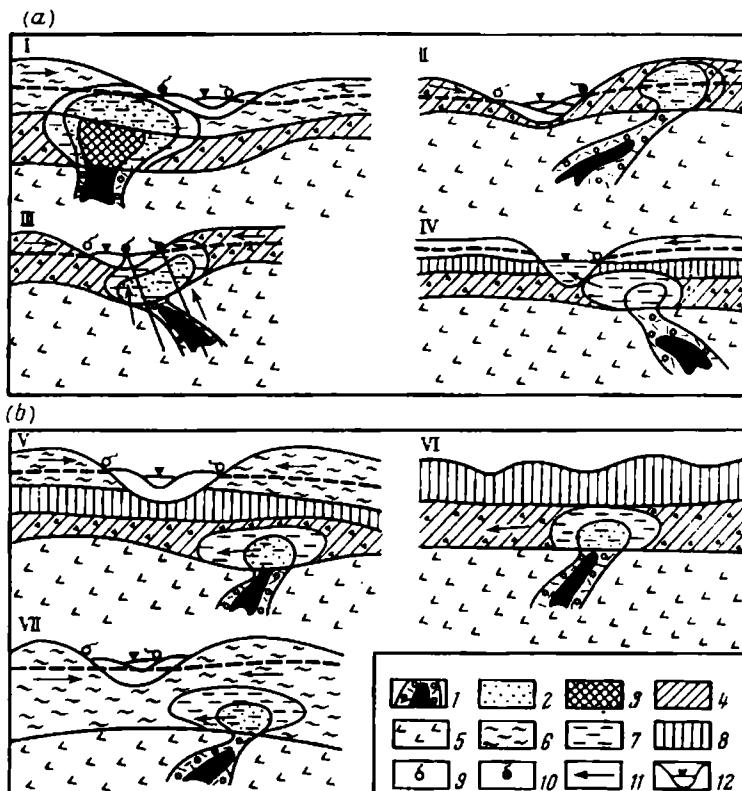
FIG. 82. Principal types of aqueous dispersion aureoles. After G.A. Goleva: a—outcropping aureoles (types I-IV); b—hidden aureoles V-VII). 1—orebody and its primary halo; 2 — secondary dispersion aureole; 3 — oxidized ores; 4 — residuum (permeable); 5 — enclosing rocks; 6 — sedimentary water-bearing rocks; 7 — aqueous dispersion aureole; 8 — aquiclude; 8, 10 — springs with background (9) and anomalous (10) ore element content; 11 — direction of water movement; 12 — local base level of erosion

cipal types of· aqueous aureoles associated with a concealed mineralization to be located by hydrochemical surveys are shown in Fig. 82. Similar data are presented in the Manual [17, Fig. 5]. Attempts are being made to conduct geochemical surveys in uncovered mountainous areas to counterbalance lithochemical surveys. Dispersion flows from ore deposit outcrops originate in mountainous areas

as a result of slope erosion and defluxion of residual dispersion aureoles formed by stable minerals of oxidized ores. The salt component of these lithochemical dispersion flows plays a subordinate role. It has been calculated that the fraction of the dissolved ore element load in the Siberian mountainous regions takes some 0.1 to 0.5% of their total load [20, 34]. For arid zone mountain streams the fraction of the dissolved load decreases by a factor of manifold. Clearly, under such conditions it is advantageous to sample the solid phase of the load for exploratory purposes.
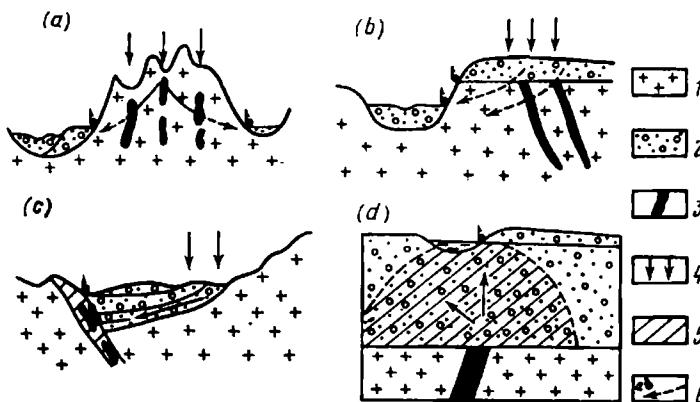
FIG. 83. V.I. Krasnikov's diagrams to prove the higher depth of hydrochemical prospecting:

a-d — different conditions of occurrence of orebodies. 1 — enclosing rocks; 2 — overlying sediments; 3 — orebodies; 4 — atmospheric precipitation; 5 — diffusional geochemical aureole; 6 — sampling points (a) and direction of movement of water (b)

As the efficacy of hydrochemical surveys is being discussed, it is not uncommon to refer to the fact that they permit exploratory effort to be directed to greater depths without taking into consideration the interrelation between hydro- and lithochemical anomalies induced by phase transitions. The thesis as to an "enhanced penetration" of the hydrochemical method of exploration was put forward by V.I. Krasnikov in 1956 and was repeatedly referred to by many other workers. Diagrams compiled by V.I. Krasnikov illustrating this enhanced penetration and published in 1959 were many times reprinted and included in textbooks for college students [22], therefore we find it necessary to consider them. V.I. Krasnikov's ideas (Fig. 83) would have been correct, had there been no interaction between natural waters and enclosing rocks. It should be pointed out, however, that throughout the channels of movement of waters, particularly, at sites of their cropping out to the ground surface as springs, processes are at work that cause the equilibrium in ore element distribution to be shifted toward a solid phase. The reactions

that underlie methods of analysis of water samples, i.e. coprecipitation with Al hydrous oxide or with $CaCO_3$, extraction involving various organic and mineral sorbents, in the natural environment are taking place continuously and spontaneously. That is why standard lithochemical sampling of the alluvium of streams, side walls and bottom of springs ensures the same results as can be obtained by hydrochemical sampling, so there are no grounds to assume the deeper penetration offered by the latter technique.

What has been said above is true for the data in Fig. 82: the outcropping aqueous aureoles of types *I-IV* can well be revealed by lithochemical sampling, so the use of the hydrochemical method of the search for ore deposits under such conditions is feasible but not reasonable. On the other hand, to detect hidden aqueous aureoles of types *V-VII*, hydrochemical sampling of subsurface waters appears to be the most reliable technique for pinpointing a hidden mineralization. Hydrochemical anomalies originate as a result of an involved process where the decisive role is being played by the dissolving action and upward migration of subsurface waters which permits deposits occurring below the modern base level to be located.

If the hydrochemical method is to be characterized, one should point out that its results are dependent on the seasonal fluctuations of the water table, atmospheric precipitation and the regime of river drainage changing hundreds of times within a short lapse of time. This is what is responsible for the inconsistency of quantitative characteristics of hydrochemical background—variable and often "zero" values of C_0, a large or unknown value of the standard factor ε, poor reproducibility and small contrast of hydrochemical anomalies. Monographs and manuals on hydrochemical prospecting do not generally present data on local values of ε, and in place of the contrast index γ they give maximum values of the concentration coefficient (K_h) calculated from the ratio of technogenic waters to background the magnitude of which is still unable to characterize the promise offered by this type of survey. All this makes difficult quantitative interpretation of a geochemical field and elaboration of reliable methods for the evaluation of prospective metal reserves through analysis of the hydrochemical anomalies.

As is known, the most important method of prospecting for ore deposits in mountainous areas is by conducting lithochemical surveys of dispersion flows at density of 1 sample per 1 km^2. The costs and results of these operations should be compared with hydrochemical surveys at the same sampling density. Testing and analysis of litho- and hydrochemical samples collected at identical sampling points fail to attest to advantages of the hydrochemical method.

The sulphate lake Gai, South Urals (pH = 1.1, copper content is up to 1 g/l), is a characteristic example of a hydrochemical anomaly indicative of a hidden copperpyrite deposit under an overburden

of Jurassic conglomerates and Paleogene Quaternary clays up to 100 m in thickness. The hydrochemical method has played a definite role in the discovery of a fifth hidden orebody of this deposit. The hidden Gai deposit is immediately overlain by a pronounced and vast superimposed lithochemical dispersion aureole that has been studied in detail by M.A. Glazovskaya. This deposit would be reliably located by lithochemical prospecting without having to resort to more sophisticated hydrochemical techniques. Sinking exploratory boreholes into the most intense hydrochemical anomaly in Central Kazakhstan known as the Jorga anomaly containing sulphur acid, copper-containing water, failed to discover economically important ore. Ten prospecting boreholes encountered only pyritized rocks with the Cu content not more than 0.1%.

The fact that the hydrochemical anomaly was pronounced in the particular case may have resulted from a relatively abundant pyritization of rocks and small amounts of atmospheric precipitation under arid conditions. The inadequacy of means of quantitative interpretation of hydrochemical anomalies representing a complex kinetic system prevents us from unambiguously evaluating the results of this prospecting by drilling boreholes. The impoverished lithochemical anomaly referred to this area was of a very moderate size.

It remains still an urgent problem to decide where it is better to apply hydrochemical techniques. No doubt, there are geological conditions under which this method is preferable. This is, in particular, true for the exploration of potassium salt deposits and, probably, bromine- and iodine-containing mineralized waters. Potassium salt deposits originate at the final stage of the development of saliferous basins, upon the deposition of thickening sea water of carbonates and calcium sulphates, most of halite and part of magnesium sulphate. Potassium salts occupy the uppermost position in the stratigraphic column and are underlain by thick halite deposits. So that the process of potassium salt deposition may be implemented, proper geological conditions are needed.

It has been found by M.G. Valyashko that the onset of these favourable conditions is indicated by a dramatic increase of the bromine to chlorine ratio $\left(\frac{Br}{Cl}\cdot 10^3\right)$ in the liquid phase of thickening brines from 3-13 units at the stage of normal halite deposition to 14-17 units at the stage of potassium salt deposition. The evaluation of this index directly from field data seems to be one of prerequisites of hydrochemical prospecting for potassium salt deposits. Potassium is one of moderately active and sluggish aqueous migrants, its aqueous migration coefficient values K_x are in the range 0, $n - n$, and the thalassophyly coefficient τ_x is 0.016 [23].

Hydrochemical methods of prospecting for hidden ore deposits still have to be elaborated, including methods of sampling waters collect-

ed in prospecting boreholes and pits excavated in allochthonous sediments and ore-bearing bedrocks. It is best to refer to hydrochemical techniques when the overburden is underlain by an aquifer and overlying sedimented layers contain aquicludes. Approximately similar conditions are illustrated in Fig. 84 showing the Talnakh copper-nickel deposit that features water-bearing glacial sandy-shingle beds overlain by impervious loams. Under such conditions the lithochemical (superimposed) dispersion aureole associated with this
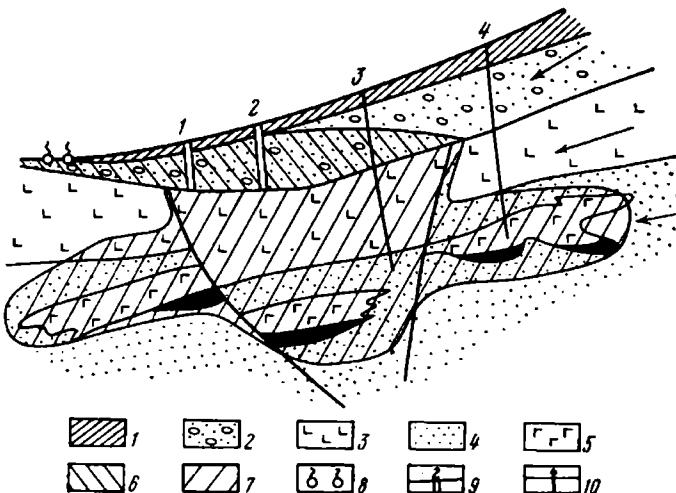
FIG. 84. Diagram illustrating the origination of aqueous dispersion aureole in Talnakh deposit. After S.L. Shvartsev:

1 — glacial water-resisting loams; 2 — glacial sandy-gravelly sediments; 3 — basalts of various composition; 4 — aleurolites, argillites, sandstones; 5 — gabbro-diabases; 6-7 — aqueous dispersion aureoles in loose sediments (6) and in bedrocks (7); 8 — springs with anomalous high heavy metal content; 9-10 — boreholes that discovered anomalous waters in loose sediments (9) and in bedrock (10)

deposit could not but be exposed at the ground surface. Note that springs shown in the left-hand side of Fig. 84 may be absent and the hydrochemical aureole can have been of a concealed type. As has already been pointed out, hydrochemical techniques of prospecting have contributed to the discovery of a copper-nickel deposit located in the same district.

Aquifers underlying the sediment cover may intensively interact with water in the fissures of the foundation, which fact yields more geochemical information when sampling in a search for hidden mineral deposits. In case the water-bearing horizons have no direct contact with atmospheric oxygen, organic or mineral colloids in the soil, the commonly flushed water-bearing quartz sands are able to shift the equilibrium in the ore element distribution toward a liquid phase.

This is what makes the geochemical environment of subsurface waters different from the conditions at the ground surface if they are discharged as natural springs.

Prospecting for bed oxidation zone deposits is a very promising domain for the hydrochemical method. Orebodies of such deposits known as rolls are formed by natural waters on a reductional barrier (Fig. 85). Oxygen-rich meteoric water, infiltrating through granite rock mass, can be enriched by hexavalent uranium, even if the ele-
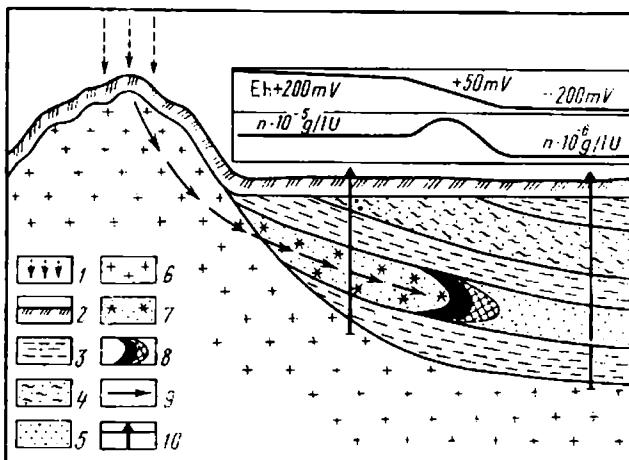
FIG. 85. Diagram of infiltration-induced deposit with graphs of Eh and U contents in stratal waters [34]:

1 — atmospheric precipitation; *2* — Quaternary sediments; *3* — clays; *4* — loams; *5* — sands; *6* — granitoids; *7* — oxidized rocks; *8* — mineralization; *9* — direction of movement of stratal waters; *10* — exploratory boreholes

ment content in these rocks only insignificantly exceeds background $(n \cdot 10^{-5}$ g/l). Upon migration to an aquiferous horizon of the sediment cover of a piedmont valley these waters use the oxygen for the oxidation of organic matter, ferrous protoxide and pyrite which are common constituents of sandy facies deposited in reduction conditions of the sea floor. At the boundary between the oxidized portion of the bed and its original state there appears a drastic change in geochemical conditions giving rise to the precipitation of tetravalent uranium at a reduction barrier ultimately resulting in the origination of economic ore deposits. The U content in the waters migrating through beds after they have passed through the reduction barrier drops by an order of magnitude, up to $n \cdot 10^{-6}$ g/l.

It is the purpose of hydrochemical prospecting to determine the interval of subsurface waters where oxidation conditions change for reduction ones followed by a drop of the U content in the waters.

This can well be achieved by drilling exploratory boreholes following the dichotomy principle accompanied by the hydrochemical sampling [34]. In a similar fashion hydrogen deposits of Mo and Se, elements with the variable valency capable to be deposited on a reduction barrier, may originate. Under such conditions the hydrochemical method of prospecting is the most convenient.

In technical terms, when hydrochemical techniques are to be used, mobility of water may be enhanced by pumping and creating cones
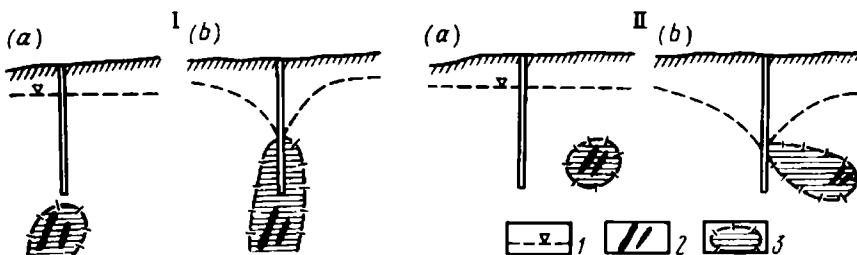
FIG. 86. Position of aqueous aureole before pumping (a) and after pumping (b). After P.A. Udodov et al.:

I — borehole that fails to penetrate mineralized zone; II — borehole drilled aside from mineralized zone; 1 — level of subsurface waters; 2 — mineralized zone; 3 — contour of aqueous dispersion aureole

of depression. As a result, waters of the hydrochemical dispersion aureole approach the borehole and are available for hydrochemical sampling (Fig. 86).

All in all, without overestimating the possibilities offered by the hydrochemical method, one must collect hydrochemical samples from whatever boreholes that may be available and enter the results in geological prospecting field records. The advent of sophisticated techniques for analyses of natural waters using ion-selective electrodes and special electronic devices with a digital readout of the observed results is likely to enhance the efficacy of the hydrochemical method.

The sampling of natural waters for exploratory purposes and preparation of samples for analysis are to meet the requirements outlined in the Manual [17]. The collection of samples from open water sources presents no problem; samples from subsurface aquifers use specially designed samplers after the boreholes have been washed and pumped.

Apart from determinations of the pH, sometimes ΣCu, Pb, Zn known as the sum of metals, of SO_4^{2-}, Cl^- and HCO_3^- contents, trace element concentration is carried out directly at the water source. This operation commonly uses methods of coprecipitation worked out at the Tomsk and Leningrad Polytechnical Institutes referred

to as "the TPI method" and "the LTI-VITR method". Concentration using the TPI method consists basically in the coprecipitation of trace elements with Al hydrous oxide in the presence of sodium sulphide, thus principal constituents of aqueous mineralization do not precipitate. The LTI-VITR method relies on the coprecipitation of trace elements with Cd sulphide in the presence of ferrous chlorine. There being some difference in the list of elements to be concentrated, the two methods precipitate Zn, Cu, Pb, Co, Sn, Ag, V, Cr, W, Sb, As, Hg, Ti, Nb, some 20 chemical elements in either case. The material is filtered out, dried and subjected to spectroscopy. Ion-exchange resins are used for precipitating Li, Rb, Cs. Direct analyses of water samples determine the total water mineralization (M), the Eh, pH, the contents of Cl^-, SO_4^{2-}, HCO_3^-, Fe_{tot}, O_2, Ca^{2+}, Mg^{2+}, H_2S and CO_2.

Sec. 5.2. The Atmochemical Method

Atmochemical prospecting (gaseous surveys) for mineral deposits consists in the investigation of the composition of the subsurface atmosphere, i.e. gases saturating the near-surface rocks and soils. If gas samples are collected from minor depths (1-3 m), this procedure is called a survey of the subsoil air. Modern gaseous surveys use sampling from 20 to 600 m. The composition of the near-surface atmosphere is analysed less commonly although it is this kind of survey that is more likely to yield the desired information more readily. Aerosol surveys seem to refer to lithochemical prospecting.

The earth's atmosphere is mainly composed by three gases, i.e. nitrogen (some 78%), oxygen (some 21%) and argon (about 1%) that make up 99.94% of its total mass. The water vapour content of the atmosphere has variable values; the CO_2 content is about 0.03%, the fraction of other gases is 10^{-4} to 10^{-6}% and less [22]. The low geochemical background and pronounced mobility of chemical elements in the gaseous phase provide most favourable conditions giving rise to atmochemical dispersion aureoles associated with any type of mineral deposits.

The atmochemical prospecting, originally known as "a gaseous survey" came into being early in the 1930s and is closely linked to the name of V.A. Sokolov [11]. As conceived by this researcher, the purpose of the method was to locate oil and natural gas fields through determinations of the gaseous hydrocarbon contents in air samples collected from the subsoil. The emanation survey techniques originated in the same time period. These consist in the determinations of the radon and thoron contents in the soil air for exploratory purposes. In the prewar years gaseous surveys were conducted with a variable degree of success in a number of oil-bearing districts, and, on a minor scale, in coal regions. The emanation survey has become an integrated part of radiometric exploration for radioactive ores.

which represents a self-contained, well elaborated field of applied geochemistry.

New aspects of the application of atmochemical exploration were to emerge later. Inspired by the ideas of A.A. Saukov, in 1956 E.A. Sergeev began to develop a gaseous mercury method [13] of hunting for ore deposits. Important contributions to this method were made by the studies of V.Z. Fursov [9], I.I. Stepanov and a number of foreign workers. It is then that attempts were first made to use atmochemical exploration for ore deposits from indirect indicator gases, such as CO_2, O_2. This method was further developed by N.N. Kulikova, A.I. Fridman, S.A. Vorob'ev, B.A. Dosanova and many others. The method of helium survey has proven successful owing to the efforts of I.N. Yanitsky and others.

The atmochemical method of exploration for solid-phase mineral deposits has passed the first experimental stage, and directions for conducting exploratory atmochemical surveys in covered ore districts have been incorporated in the acting Manual [17]. Much interest is being aroused by atmochemical exploration for hidden ore deposits in foreign countries as well [5]. Atmochemical prospecting of various detail in oil- and gas-bearing regions have become an important aspect in the complex of prospecting operations due to the many years of efforts by P.L. Antonov, V.A. Sokolov, L.M. Zor'kin, S.L. Zubairaev, A.V. Petukhov and many other workers [2, 11, 12].

From the geological and geochemical viewpoint, atmochemical prospecting for oil and gas is easy to account for. A natural oil deposit is a mixture of liquid and gaseous hydrocarbons (HC), methane, naphthene and aromatic series with an admixture of sulphurous, nitrous, oxygen-containing compounds and ash residues. Depending on the geological setting, it may represent either a one-phase gas-saturated liquid or separated into a liquid and a gaseous phase giving rise to what is known as a gas-cap in the upper horizons of the deposit. The composition of oil gas is mainly due to methane (CH_4) and its heavy homologues—ethane, propane, butane whose common formula is C_nH_{2n+2}. Other constituents are variable amounts of nitrogen, carbonic acid, helium and other gases, the methane content generally exceeding the total content of heavy hydrocarbons (HHC). Fuel gas deposits and coal deposit gases are of a similar composition.

The hydrocarbon content in oil gas amounts to 80-95%, whereas their geochemical background in the subsoil air is not more than 2 to 4×10^{-4}%. It is this large difference in concentration that is responsible for the dispersion of hydrocarbons in the enclosing rocks. Any rock species is liable to the penetration of gases for it always displays porosity or jointing. Lithostatical pressure causes gases in free pores and fissures to move toward the ground surface (effusion). The dispersion of gas in water-saturated rocks is due to diffusion and is determined by the concentration gradient.

Figure 87 presents an elementary diagram of the formation of an atmochemical dispersion aureolo associated with an oil and gas deposit. It shows two versions of plots of the hydrocarbon content in the subsoil atmosphere: one having a peak (high) over the deposit indicative of the so-called direct anomaly; and the other having two peaks separated by close-to-background values at the epicenter of the deposit. The latter case, when viewed in plan, shows ring-shaped anomalies very often met with in practice. This shape of gaseous anomalies results from pronounced jointing of rocks close to a pericline and weaker in the dome portion of the structure. Similar gaseous aureoles are associated with deposits of helium, carbonic acid, sulphur gas and other natural gas assemblages trapped in the lithosphere. The He content in helium deposits may amount to 6-8%, given the clarke of the atmosphere equal to $5.2 \times 10^{-4}\%$ He, in carbon dioxide deposits its content attains 99%, given the clarke of the atmosphere of $3 \times 10^{-2}\%$ CO_2. The hydrogen content in gaseous emanations may amount to 50% at background values in the soil air equal to $2.1 \times 10^{-4}\%$ H_2 etc. That is why the atmochemical method makes it possible to directly locate oil and gas deposits.

FIG. 87. Atmochemical dispersion aureole from oil and gas deposit:
1 — overlying sediments; 2 — productive strata; 3 — oil; 4 — gaseous cap; 5 — direction of gaseous effusion and diffusion; 6 — gaseous survey boreholes and graphs of hydrocarbon contents (two versions)

Gaseous mercury surveys provide indirect techniques of exploration for mineral deposits. It is only for mercury deposits that they may be used as a direct method of exploration. The close geochemical affinity of mercury to sulphur is what refers the former to the chalcophile group of elements (Cu, Ag, Au, Zn, Cd, Hg, In, Tl, Ge, Sn, Pb, As, Sb, Bi, S, Se, Te). Appreciably large mercury contents can be found in sulphide minerals and deposits of elements of this group. For example, the Hg content in cerussite—the product of oxidation of galena—may be up to 0.1% which exceeds by a factor of tens of thousand the clarko of the lithosphere. The potency of mercury to accumulate is being also displayed by other mineral deposits including oil and gas fields. The other remarkable properties of mercury

are pronounced volatility and potency to reduce under supergene conditions to the native state passing to the state of atomic gas by means of direct sublimation from natural compounds.

All this, coupled to very low (1.33×10^{-9} mg/l) and stable ($\varepsilon = 1.02$) geochemical background of Hg in the atmosphere is what makes gaseous mercury surveys an important and, perhaps, versatile method of geochemical exploration for mineral deposits in covered regions. Figure 88 presents a diagram of a gaseous mercury survey over a hidden gold ore deposit. Here, under conditions of a loess loam overburden 40 m in thickness, an anomaly was discovered in the soil air, whereas the Hg content in lithochemical samples remained equal to background [9].

The promise offered by this method has not completely shown itself. The principles of atmochemical exploration for ore deposits by referring to the complex of indicator gases have yet to be understood.

The impressive bulk of available evidence strongly suggests that ore deposits are enclosed in a specific gaseous atmosphere throughout the period of their existence. Systematized data on the composition of these gases can be found in works by A. I. Kravtsov, A. I. Fridman [8], much information has been obtained by S.A. Vorob'ev. Ore mineral deposit gases may be divided into three main groups: (1) gases syngenetic to the ore formation process; (2) gaseous components of tectonic disturbance zones; (3) gases formed in supergene processes. Gaseous components of ore formation are trapped in inclusions of ore and gangue minerals making up ore deposits. For a vast group of hydrothermal deposits these include carbon dioxide, hydrogen sulphide, sulphur dioxide, methane, hydrogen, volatile halogen compounds and other gases the presence of which in orebodies has been proved by the numerous studies of gaseous-liquid inclusions in minerals. The most common constituent of an ore forming environment is carbon dioxide which can be found in appreciable amounts in most of gas-

FIG. 88. Comparative results of gaseous mercury and lithochemical surveys over a hidden gold ore deposit. Uzbekistan [8]:

1 — loessial loams; 2 — andesite-dacite porphyrites; 3 — diabase porphyrite dykes; 4 — quartz sulphide gold orebodies (fahlores, pyrite, chalcopyrite); 5 — clay and breccia; 6 — tectonic disturbances; 7 — Hg contents in loose sediments (in %); 8 — mercury vapours

eous-liquid inclusions. Carbon dioxide and hydrogen trapped in ore minerals are products of chemical reactions taking place in the magma [8], they result from the interaction of carbon with water vapours: $C + 2H_2O = CO_2 + 2H_2$. Hydrogen is believed to originate also from water vapours interacting with iron oxides: $3FeO + H_2O = Fe_3O_4 + H_2$. Increased H values are typical of high-temperature hydrothermal deposits.

Methane may form in the deeper reaches of the earth crust upon the interaction of carbon dioxide with molecular hydrogen in an appropriate physicochemical environment ($T = 600°$, $P = 104$ kPa). In the presence of catalysts, the reaction may occur at 475 °C:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$
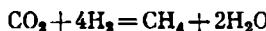
Other schemes of reactions are possible:

$$C + 2H_2 = CH_4$$
$$CO + 6H_2 = CH_4 + H_2O$$
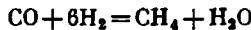
The above reactions describe the way carbon dioxide, hydrogen and methane are formed in igneous and hydrothermal processes. These substances form in large amounts during the thermometamorphism of organic matter scattered in the enclosing rocks. The hypogene gas constituents trapped in ore material and ore-bearing rocks are continuously liberated as gaseous-liquid inclusions are uncovered by weathering, dynamometamorphism and other extraneous factors.

The second group includes gases of deep-seated origin migrating through ore-controlling tectonic zones where orebodies are confined. These gases (CO_2, CH_4, He, H_2) are products of igneous processes and chemical and nuclear reactions taking place in the earth's bowels. Their origin is similar to that of the first group gases and, if orebodies are located in the fracture zones, form an integral form of these. A typical example of this connection can be provided by the gaseous emanations from the gold-ore field Balei. According to the data submitted by N.N. Kulikova, gas almost completely composed of CO_2 was observed to exude here. The high content of CO_2, CH_4 and other gas species in the air of many mines is evidence attesting to the constant discharge of large amounts of natural gas to the subsurface atmosphere.

Intensive gas emanations composed by CH_4 (99 %) and CO_2 (1 %) were recorded as copper-nickel deposits in the Norilsk district were being mined. Continuous (lasting for 6-7 years) gas emanations from some exploratory boreholes were observed at the Urupskoe copper-pyrite deposit. The composition of the gaseous flux with high contents of carbon dioxide, methane, helium and hydrogen sulphide practically did not change as long as the gas emanated [8]. In his popular monograph "Mineralogy" A.G. Betekhtin reports high-intensity emanation of H_2S jointly with CO_2 and AsH_3 as orpiment

ores in the Julfa deposit were being mined. The emanation of gas that contained CO_2 (67.9%) and CH_4 (8.6%) was recorded at the Nadezhdinskoe deposit.

The third group includes gas species that result from processes taking place in the supergene zone of ore deposits. Physicochemical transformations of ore minerals are particularly pronounced in the oxidation zone of massive sulphide deposits (cf. Sec. 3.4). The resultant free sulphuric acid and acidulous metal sulphates, in the presence of carbonates or carbonate waters, react to liberate free carbon dioxide.
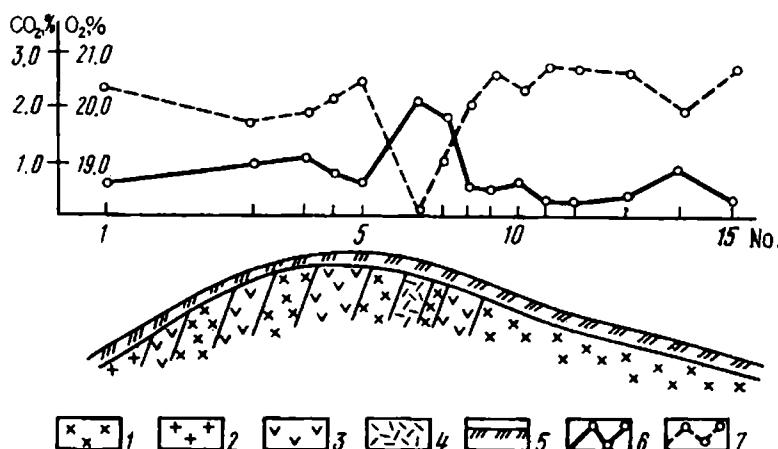
FIG. 89. Gaseous aureole over pyritization zone. After V.S. and S.S. Glebovsky: 1 — gneisses; 2 — granites; 3 — quartz porphyrys; 4 — pyritization zone; 5 — loose formations; 6, 7 — graphs showing contents of CO_2 (6), O_2 (7). Sampling depth: 1.5 m

The reaction of sulphuric acid with such sulphide minerals as pyrite, galena, sphalerite and others at a low fractional oxygen pressure gives rise to hydrogen sulphide according to the scheme: $MeS +$ $+ H_2SO_4 \rightarrow MeSO_4 + H_2S$.

Sulphuric gas is produced as melanterite reacts with pyrite if free oxygen is available.

Oxidation of pyrites requires large amounts of free oxygen. It has been estimated by V. S. Glebovsky and S. S. Glebovsky that it takes a pyrite lode 1 m^2 in area up to 3.5 m^3 of free oxygen to oxidize a 1 mm thick layer forming $Fe(OH)_3$ and H_2SO_4. Such great quantities of oxygen result in a marked drop in its content in the subsoil air over oxidizing massive sulphide deposits.

Gases of all the three groups taken together are responsible for the origination of multicomponent atmochemical dispersion aureoles associated with ore deposits; field observations show that they can easily be detected. Figure 89 presents the results of the atmochemical

survey along a profile cutting a pyritization zone over which anomalous increased CO_2 contents and diminished O_2 contents have been discovered. These early results were of methodological value. In practical terms atmochemical surveys are plausible only in covered regions; examples illustrating such operations are presented in Chapter 6.

Convincing results of atmochemical surveys have been obtained by A.I. Fridman (Fig. 90). Anomalous CO_2 contents of up to 4.5%
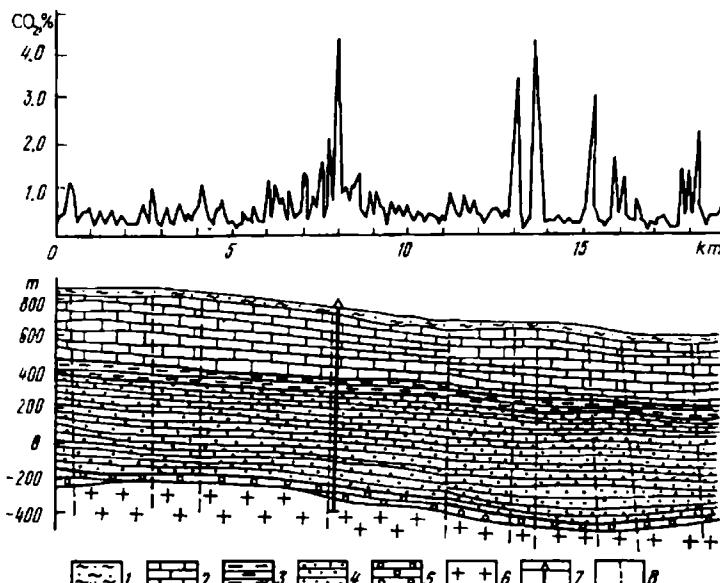
FIG. 90. Graph of CO_2 contents and geological section along a profile Borgustan-Essentuki. After A.I. Fridman:

1 — Quaternary loams, clays; Cretaceous sediments; 2 — limestones; 3 — argillites; 4 — sandstones; 5 — Jurassic conglomerates; 6 — granites; 7 — borehole; 8 — faults determined from results of an atmochemical survey

for local background equal to 0.33% CO_2 have been discovered on a profile Borgustan-Essentuki by sampling at an interval 100 m and depth 1.5 m. Basing on these data, a borehole drilled into one of the anomalies located a carbon dioxide deposit at a pressure of about 60 kPa at a depth 600 m. CO_2, CH_4, H_2, He gaseous anomalies have been discovered by atmochemical surveys for various mineral deposits, so their existence poses no problem.

Table 19 presents selected data on the results of atmochemical studies.

The theory of the origination of gaseous dispersion aureoles depends on a consideration of differential equations of diffusion in a horizon-

TABLE 19

Characteristics of Indicator Gases

Description of deposit	Gas	Geochemical background		$c_{max}*$, %	Contrast index γ
		c_0, %	$\varepsilon^{\pm 1}$		
Ore deposits	CO_2	0.3	1.5	3.0	5.68
and kimber-	CH_4	1.3×10^{-4}	1.5	0.01	10.7
lites	H_2	2.1×10^{-4}	2.0	0.01	5.57
	O_2	20.6 ± 0.21	—	15.0	26.7
Mineral waters	CO_2	0.33	2.38	4.5	3.01
	O_2	20.4	1.01	17.3	16.5
Oil and gas	CH_4	0.25**	2.1	1.57**	2.5
	HHC	0.01**	1.6	0.14**	5.6

* For O_2, c_{min} is given
** Expressed in cm^3/kg

tal layered medium. Viewed from a methodological standpoint, of most importance is to roughly estimate the distance H_0 at which the gas content in the subsurface atmosphere will represent a definite fraction of that in the deposit of the useful component (C_p) if the diffusion process occurs during a time period T in a medium whose diffusion coefficient is D. The solution of this problem presented in theoretical physics courses is found from the relationship

$$C_z = \frac{C_p}{Ei\left[-\frac{H_0^2}{4DT}\right]} Ei\left[-\frac{(H_0+z)^2}{4DT}\right] \qquad (108)$$

where C_z is gas concentration along the aureole axis at depth z; Ei is an integral exponential function of the bracketed term. Values of this function can be found in mathematical handbooks. By proceeding from close values of diffusion coefficients for CO_2 and CH_4 evaluated by the magnitude of $D = (1 - 5) \times 10^{-6}$ cm^2/s and using Eq. (108), S.A. Vorob'ev calculated the expected results of diffusion during the time interval corresponding to the geological age of the adjacent stratigraphic units of the sediment cover (Table 20). The CO_2 and CH_4 contents in emanations from ore may attain 0.5-5% [8], and in gas deposits approach 100%, therefore the data obtained strongly suggest that it is possible to discover gaseous anomalies over concealed deposits even though the thickness of the overburden may run into tens to thousands of metres. This range of depths fully agrees with the distance from the ground surface to which exploratory effort to locate hidden ore deposits is being currently directed (500 m).

TABLE 20

Thickness of Overburden H_0 (in m) at which CO_2 and CH_4 Anomalies
(Linear Source) May be Expected at the Upper Surface. (After S. A. Vorob'ev)

Description of sediments	Age, mlns of years	C_{max} in fractions of C_p			
		0.001	0.01	0.05	0.2
Holocene	0.01	55	43	33	23
Quaternary	0.7	403	290	196	103
	1.7	618	430	290	140
Neogene	25	2280	1570	970	400
Paleogene	67	3680	2510	1520	580
Cretaceous	137	5200	3540	2120	780

If the thickness of overburden is greater, the sediments are generally
of a more ancient origin.

Similar results are obtained by calculations using a relationship
for deposits of isometric shapes whose planimetric configuration is
like that of gas deposits or ore stockwork lodes. Analogous data have
been obtained by A.P. Antonov. The formation of gaseous diffusion
aureoles is complicated in actual conditions by the inhomogeneity
in the lithological composition of the overburden, presence of water-
bearing layers and tectonic dislocations. It has recently been sug-
gested that gaseous dispersion aureoles are mainly due to the effu-
sion of gases through fissures, diffusion playing a subordinate role.
This hypothesis is validated by ring-shaped anomalies over oil-
bearing structures (see Fig. 87). However, it is diffusion that is re-
sponsible for the fact that a gaseous flow penetrates aquiferous hori-
zons.

There were many obstacles to the development of atmochemical
prospecting for mineral deposits which have not yet been completely
eliminated. Two principal operations involved, i.e. field sampling
and prompt analysis of samples collect major methodological prob-
lems for atmochemical surveys.

Gas samples are collected from boreholes at a depth below the level
of active exchange of the soil air with the atmosphere. This level is
shown by special studies to be 1.5 m. When prospecting for ore de-
posits samples are collected from a depth 3.0 m; during exploration for
oil and gas fields, from 20-25, sometimes more than 200 m. Surveys
aimed at locating oil deposits take core samples which are hermeti-
cally sealed and then degassed in the laboratory to analyse the gases
they contain.

When prospecting for ore deposits samples of free subsoil air are
collected in special 250 ml ampoules (Fig. 91). This requires that the

borehole bottom be isolated from the atmosphere and first portions of the air not representing the composition of the subsurface gases be removed from the pre-stope chamber. The volume of the air from a borehole for filling the ampoule should not be less than five times the volume of the pre-stope chamber. Care must be taken not to allow the atmospheric air to penetrate the evacuation zone (shown in Fig. 91 by a dashed line) through the borehole. When prospecting
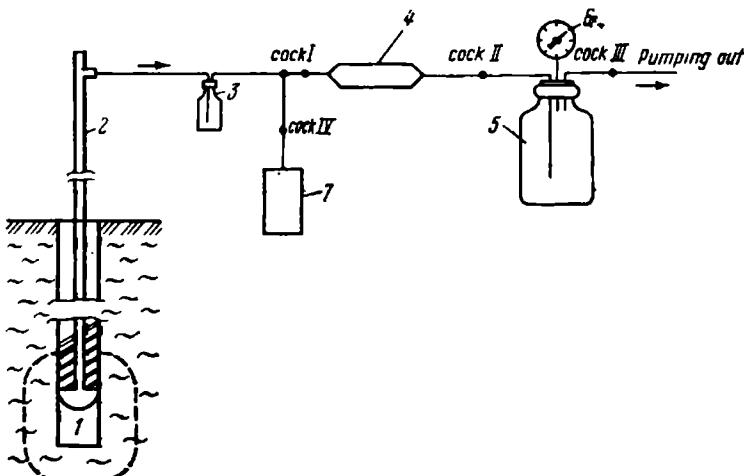
FIG. 91. Diagram illustrating gaseous sampling. After S.A. Vorob'ev:
1 — pre-stope chamber; 2 — gas sampler; 3 —[filter; 4 — gas ampoule; 5 — receivers; 6 — vacuum gauge; 7 — CO₂ gas analyser; I-IV — gas cocks

for solid-state mineral deposits gas samples are collected to determine the CO_2 content by using a mine interferometer. The other gas constituents and repeatedly the CO_2 content are determined by laboratory analysis.

Sampling in gaseous mercury surveys is done by a special probe with an Au sorbent. Once the specified volume of the soil air has been pumped, the absorbed mercury is sublimated by heating the sorbent with electrical current followed by field analysis.

In the first decades of conducting gaseous surveys for locating oil fields prospecting operations were inhibited by the complexity and insufficient accuracy of gas analysis. The advent of methods of chromatographic analysis has first enabled atmochemical surveys to be used more extensively for locating deposits of various minerals.

In chromatographic analysis (Fig. 92) a flux of inert carrier gas is passed at a constant rate through a sorbent-filled dividing column. Some 2-5 cm³ of the gas mixture to be analysed is introduced in the flux by using metering injector. The sample is divided into its con-

stituents A, B and C due to the different physicochemical properties of these latter and multiple repetition of elementary acts of sorption and desorption. The gaseous constituents thus travel at different rates in the dividing column to come individually to the detector. Combustible constituents are determined by burning them from the heating or ionization effect; noncombustible ones, from thermal conductivity or optical properties. The current in the detector circuit is registered by a recording potentiometer.

Atmochemical exploration, mainly for oil and gas fields, is expected to be further developed by the laser gas analysers of methane and
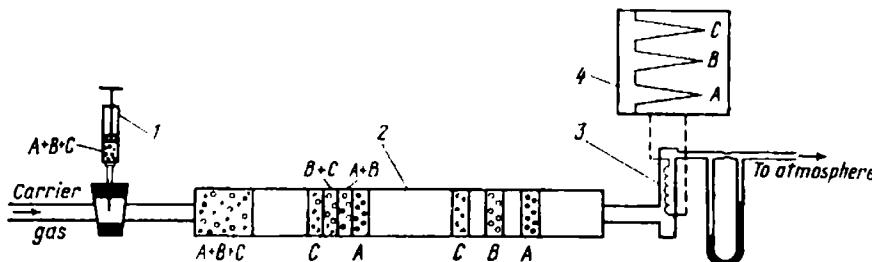
FIG. 92. Chromatographic gas analysis:
1 — gas metering injector; *2* — dividing column filled with a sorbent; *3* — detector; *4* — recording potentiometer. *A*, *B*, *C* — constituents of test gas

other gases, including aerial and automobile surveys involving studies of the near-surface atmosphere. Special helium surveys use portable magnetic discharge devices model ИНГЕМ-1. New promise is offered by atmochemical exploration for ore deposits due to the recent works of Czech geochemists who have elaborated methods to determine the Zn, Pb, Cu and F contents in the soil air [21].

Clearly, the principal application of the atmochemical method will still consist in exploration for petroleum and gas deposits. Section 6.3 briefly outlines these aspects of geochemical prospecting. Atmochemical surveys for ore deposits in covered areas seem most likely to be used on a wider scale compared with hydro- and biogeochemical prospecting.

Sec. 5.3. The Biogeochemical Method

This method relies on studies of the composition of living matter, generally, that of plants. No doubt, there is an intimate connection between the chemical composition of living matter and that of its environment which in extreme cases is manifested by a change in species, enhanced or suppressed development and appearance of specific morphological features. References to the connection between the geological structure of a terrain, the presence of mineral deposits and

the composition of vegetation were made as early as medieval liter-
ature on mining. Modern biogeochemical prospecting depends on
chemical analyses of the material, studies of the spectrum of species
and morphological properties of vegetation being the object of geo-
botanical studies. Similarly to microbiological surveys which study
the species composition of bacteria in the soil for prospecting purposes,
geobotanical methods cannot be considered to be geochemical and
are not discussed here.

In modern time an interest in biogeochemical prospecting for min-
eral deposits was aroused in the mid-1930s following early studies
of lithochemical dispersion aureoles [29]. The biogeochemical meth-
od of prospecting was developed by S.M. Tkalich, A.P. Vinogra-
dov, D.P. Malyuga, V.V. Polikarpochkin, A.L. Kovalevsky in
the USSR [13, 24], by N. Brundin and S. Palmqvist in Sweden,
H.V. Warren and R.E. Delavault in Canada, H.L. Cannon in the
USA, R.R. Brooks in New Zealand and by other geologists.

Investigations invariably discovered the availability of biogeo-
chemical anomalies in the chemical composition of plants growing
over deposits of copper, zink, lead, uranium, molybdenum, nickel,
boron, gold and other metals. These biogeochemical surveys gene-
rally consisted in the study of one or more dominant species of plants,
reduction to ashes of the plant material and spectral analysis of the
plant ash.

The connection between the chemical composition of the soil and
that of vegetation growing on it is of an involved character. The frac-
tion of animal organisms is negligible compared with the total bio-
mass of the earth, and clarkes of the biosphere fairly closely approxi-
mate the average chemical composition of vegetation. As can be
seen from Table 1, the first ten chemical elements, taken together,
make up 99.96 % of the biosphere, and the first three major elements—
O, C and H—constitute 98.5 % of the entire biomass. The fraction of
the remaining 82 minor elements is only 0.04% of living matter.
More than 50 % of the mass of living matter is composed by water
which binds appreciable amounts of oxygen and hydrogen. Gaseous
components of the biosphere taken from the atmosphere are returned
to this latter in the course of the biological cycle of matter.

It has been suggested by B.B. Polynov to characterize the geo-
logical role of biogenic migration of trace elements by the ratio be-
tween the element content in the plant ash and that in the soil on which
it grows. This index is known as a coefficient of biological absorption
denoted by A_x:

$$A_x = \frac{C_2}{C_1} \qquad (109)$$

where C_2 is the element content in the plant ash, %; C_1 is the element
content in the soil, % [23].

Much information on the trace element contents in plants, animals and soils is provided by V.V. Dobrovol'sky. The data presented in Table 21 show that for ore elements excepting Ti, Be, Sb the coefficients A_x are greater than unity which points to their capacity to accumulate in the upper soil horizons due to mineralization of annual defoliation.

TABLE 21

Average Metal Contents in Plant Ash

Element	$C_2 \times 10^{-4}$ %	A_x	Element	$C_2 \times 10^{-4}$ %	A_x
Mn	4 800	6.86	Mo	12	9.23
Zn	1 000	19.6	Sn	5	1.85
Ti	650	0.2	As	3	1.58
Cu	200	9.09	Be	2	0.80
Pb	50	3.73	Ag	0.6	12.5
Ni	40	1.54	Hg	0.25	7.58
Co	20	2.74	Sb	0.1	0.5

The ashes of plants growing over mineralizations, on spoil bank with high metal contents in soil, showed the ore element contents tens and hundreds of times more than their average level. The greatest potency to accumulate metals is manifested by certain plant species whose ash may show contents of some metals equal to some percent, e.g. more than 20% Zn, up to 8% Ni, more than 1% Cu, Pb, As, Be. However, such indicator plants are not universally distributed, they may accumulate metals even given background contents in the soil and generally are of little use for biogeochemical prospecting. Most promise may be expected from testing such vegetable species the ash of which shows low yet measurable contents of indicator elements in the background level areas that rapidly increase to attain anomalous values in the vicinity of a deposit. Hence a need to accurately evaluate parameters of local background, C_0 and ε, and the lowest anomalous content of ore elements $(C_{A,m} = C_0 \varepsilon^3 / V^{\overline{m}})$ in the ash of the local plant species and to select one or two of these for prospecting.

The relationship between the ore element contents in the habitation environment and in the plant ash is determined by their species and varies for different parts of a plant as a function of the age and phase of development. In the general case this is a complex, often nonlinear relationship governed by the properties of the element in question and largely depends on its absolute content in the soil. Two types of relationship have been established (Fig. 93). The first type approximately corresponds to a linear increase of the ore element contents in the plant ash directly related to an increase of its contents

in the soil. These plants can well be used for sampling when conduct-
ing biogeochemical prospecting to locate a deposit of the particular
element. The second type is characterized by a proportional relation-
ship between the metal content in the soil and that in the plant ash
at its low contents only. Under conditions of anomalous high metal
contents in the soil there is a progressive drop in the values of the
coefficient of biological absorption, such as to result in a negative
correlation between C_1 and C_2. This relationship is accounted for
by the protective physiological barriers in these plants that prevent
excessive amounts of one chemi-
cal element or another from pen-
etrating into the plant. Plant
species that exhibit such barriers
with background contents of ore
elements are of no use for biogeo-
chemical prospecting. The level
of increased element contents at
which the biochemical barrier
reveals itself is different for vari-
ous species and parts of plants.
It is lower for leaves and
branches and much higher for the
bark and roots of plants. A list
of objects of biogeochemical pros-
pecting of different importance
with respect to particular ore
elements is given in the Manual
[17].
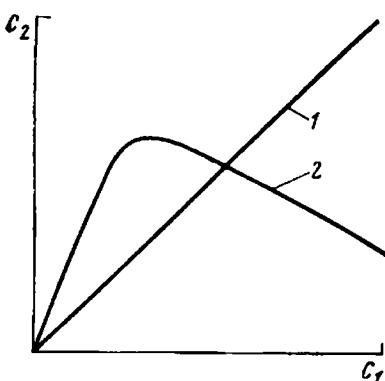
FIG. 93. Graphs of relationship be-
tween ore element content in plant
ash (C_2) and ore element content in
soil (C_1):
1 — proportional biological absorption; *2* -
presence of biological barrier

A second feature responsible
for a possible efficacy of the bio-
geochemical method of prospecting is the depth to which the root
system penetrates. As a rule, this depth is the least in permafrost re-
gions, moderate in a humid climate and greatest in arid areas varying
from 0.2-1.0 m in the northern zone to 20 m in the southern regions.
For individual plant species with a well developed root system it
may attain appreciable values, being 25 m for *Artemisia*, 37 m for
Haloxylon, 40 m for camelthorn *Alhagi* and up to 70 m for some plant
species growing abroad.

The results of biogeochemical surveys can still be evaluated in
qualitative terms only which inhibits the solution of the principal
question as to whether this method is preferable compared with other
methods of geochemical exploration. The acting manual for geochem-
ical methods of exploration for ore deposits states that it is unrea-
sonable to apply biogeochemical methods "in mountainous, inten-
sively eroded regions of whatever climatic zones as well as in other
regions that feature outcrops of primary halo and secondary litho-

chemical dispersion aureoles" [17]. It is not plausible to conduct bio-geochemical surveys in covered areas where the thickness of allo-chthonous sediments overlying an ore-bearing stratum is known to exceed the depth reached by plant root systems. According to the Manual, the biogeochemical method can well be used in covered areas of the humid zone with the overburden 2-10 m in thickness. However, abundant vegetation grown under conditions of ample wetting within the geological time span has given rise to mineralization of annual litter responsible for huge amounts of ash residues in the soil. If we assume that the present climate and vegetation date back to the early Holocene period (10 thousand years ago) we may expect a mobile equilibrium to have established between the ore element content in the soil and that in the plant ash. Moreover, if the overburden is of that small thickness, then, apart from the biogenic component, one may well expect to discover outcrops of the mechanical and salt components of the superimposed dispersion aureole resulting from the diffusion of the mineral components of the mineralization. Under such conditions lithochemical surveys are better.

The biogeochemical method is more convenient in covered ore-bearing regions in desert and semidesert landscapes of the arid zone. Deeply reaching root system and scarce vegetation permit the assumption that there is a discrepancy between the ore element contents in the plant ash and in the upper layers of allochthonous sediments to be tested by terrestrial lithochemical surveys. Given the thickness of the overburden 40-50 m and background metal contents in litho-chemical samples distinct biogeochemical anomalies over hidden ore deposits may originate.

An example shown in Fig. 94 illustrates the advantage offered by the biogeochemical method of prospecting at a flank of the Uzun-zhal, Central Kazakhstan, polymetallic deposit. This deposit has been located by lithochemical prospecting referred to a secondary residual dispersion aureole of Pb contouring the orebody cropping out at the modern ground surface (cf. Sec. 6.2.2). The major part of the mineralized zone is overlain by Neogene-Quaternary sediments 40-50 m in thickness at the upper surface of which routine lithochem-ical surveys failed to discover a superimposed dispersion aureole. The lithochemical aureole encloses only a small southern portion of the lode where there is no allochthonous sediment cover. The 0.005 % Pb isoconcentration line of the biogeochemical dispersion aureole contours the whole of the lode. The Pb content in biogeo-chemical samples over the hidden north-western part of the deposit was 0.07 % Pb background contents in the soil being about 2×10^{-3} %. The area of the biogeochemical anomaly is 5-6 times the total area of the orebody cropping out at the surface of the bedrock, the maxi-mum Pb content in the biogeochemical dispersion aureole in the open part of the lithochemical aureole was 1 % (with 1.25 % Pb in

the soil). Biogeochemical prospecting involved *Artemisia*, the plant ash sample was obtained in an oven at 500-550°. It should be noted that special lithochemical surveys followed by multiplication and averaging of the data to discover superimposed dispersion aureoles were not conducted at that time.
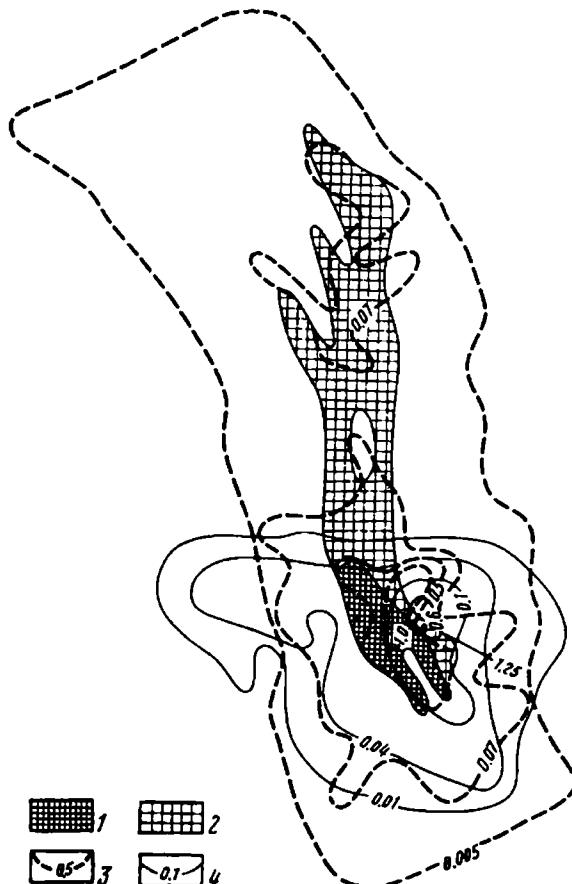
FIG. 94. Comparative results of litho- and biogeochemical surveys at Uzunjal deposit. After V.O. Getmanchuk:

orebody outcrop: *1* — to ground surface; *2* — under cover of Neogene-Quaternary sediments; Pb isoconcentration contour lines (in %): *3* — in plant ash; *4* — in soil

Most of biogeochemical surveys were carried out by different workers in uncovered ore regions where residual lithochemical dispersion aureoles in the eluvio-deluvium were available. Under such conditions it is not reasonable to use the biogeochemical method of prospecting even though anomalous ore element contents in the plant

ash may be found. To substantiate the application of the biogeochemical method of ore exploration reference is often made to a strong positive correlation between the anomalous metal contents in the soil and in the plants. However, this very circumstance attests to the disadvantage of the biogeochemical method for similar exploratory evidence more reliably interpreted may be secured by lithochemical exploration at lower costs.

Thus we may consider the principal criterion of the efficacy of the biogeochemical method of prospecting is the absence of a statistically significant correlation between the anomalous metal contents in plants and in samples collected during lithochemical prospecting over concealed ore deposits. Such conditions may originate in covered ore regions, in particular, in arid zone landscapes, in bogged up areas, in the presence of glacial moraine sediments and in other specific cases. The spectrum of these conditions, limiting values of the thickness of the allochthonous sedimented cover and vegetation types suitable for biogeochemical prospecting have not as yet been sufficiently studied.

In these recent years the biogeochemical method has been in use in the Buryat Autonomous SSR. According to E. F. Zhbanov, up to 10% of area here is blanketed by aeolian sediments from 2 to 50 m in thickness due to which fact the residual lithochemical dispersion aureoles associated with ore deposits become concealed and discovery of superimposed lithochemical aureoles is problematic. In terms of the landscape features this region refers to a mountain taiga zone.

Reconnaissance biogeochemical surveys were made in Buryatia on a 1 : 50 000 scale using a 500 by 50 m grid, in part a 200 by 20 m grid; bark and cones of pine were sampled; spectral analysis of vegetation was done by using the plant ash. By checking a biogeochemical anomaly with the Mo content in the ash 0.01% the Zharchikhinskoe Mo ore deposit was discovered. A lithochemical survey of this deposit revealed only a weak anomaly which could have well been omitted. The discovery of the Zharchikhinskoe stockwork deposit is the first important achievement of the biogeochemical method during the time period it has been used in the USSR. In his two recent papers V.G. Orlov provides convincing proofs disputing the role played by the biogeochemical method in the discovery of the Zharchikhinskoe deposit.

Sampling in biogeochemical prospecting should be referred to standard characteristics of the same species, same organ and same phenological phase of the plants being tested. The most commonly occurring species should be selected for sampling, such as possess a deeply reaching root system and have no barriers to ore element contents in the soil layer penetrated by roots [17]. If it becomes necessary to change the plant species, extend time intervals between tests, and in other cases where standard conditions of a survey are disturbed,

one must collect samples twice from at least 30-50 sampling points. Correction coefficients obtained from these data make it possible to reduce surveys made to the same level. The weight of an air-dried plant sample is generally 30-40 g, which permits spectroscopic analysis of plant ash to be done. Nuclear physical methods may be used to analyse biogeochemical samples without ashing, but experience in this field is still scarce.

Attempts to conduct biogeochemical surveys by studying ore element contents in the liver of trout (H.V. Warren and others, Canada), such as previous studies of the liver of toad in the South Urals (cf. Sec. 1.7) should be disregarded.

Sec. 6.1. General Principles

The proven efficacy of geochemical exploration for various purposes enables us to consider long-term national surveys are to be made universally on increasingly larger scales. Depending on the geological setting, the degree of exploration and economical development of the terrain, the techniques, priorities and detail of geochemical exploration may appreciably differ from one survey to another.

In terms of the aims in mind, three principal types of terrain may be distinguished:

I—mountainous folded structures and elevated shields of ancient origin made up by different-age sedimentary, igneous and metamorphic rocks subjected to multiple tectonic and magmatic activation featuring a complex of ore and other mineral components, mainly under subvertical conditions of occurrence, overlain by a cover of eluvio-deluvium of the same origin and a limited amount of allochthonous sediments ("uncovered areas");

II—flat country with overburden of recent origin up to 500 m in thickness overlying a folded foundation ("covered areas");

III—regions of long-term accumulation of different-age sedimented strata of appreciable thickness with a complex of diversified primary sedimented and epigenetic deposits, mainly under conditions of subhorizontal occurrence, including oil and gas fields, deposits of coal, sedimentary iron ores, all kinds of placer, construction material deposits etc., the depth of occurrence of the folded foundation exceeding the one that can be reached by the available mining techniques.

Targets of search in type I regions are deposits occurring in folded complex rocks; in type II regions, deposits emplaced in rocks of the sedimented cover and foundation; in type III regions, only deposits to be found in sediment cover rocks. Accordingly, the mineral species and methods of exploration vary.

As has been estimated by V.I. Krasnikov, type I regions occupy 30% of the area of the USSR; type II regions, 13%; type III regions, 57%. Figure 95 represents a simplified geological cross section that agrees to actual conditions. Starting from the USSR-China boundary in regions of North Kirghizia, across mountainous structures of the Tien Shan and Kazakh isolated hill region moving approximately along the meridian 75°, we come to covered ore-bearing territory of

North Kazakhstan, then to immense plains of the West Siberian lowland with its oil and gas fields. A similar geological cross section may be observed on a meridional profile started at the Greater Caucasian range, then passing to the Russian lowland as on latitudinal profiles from the North and Polar Urals eastward or westward.

Clearly, different geological tasks may be solved by airborne geochemical surveys on increasingly larger scales covering the entire territory of a country. In uncovered type I regions geochemical pro-
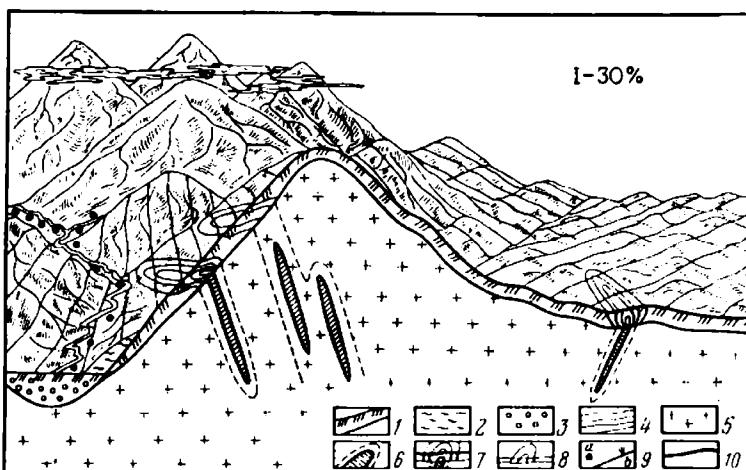
FIG. 95. Zoning the USSR territory according to conditions of geochemical pro-
1 — modern eluvio-deluvium and ancient residuum; 2 — loess-like loams; 3 — alluvium; halos; 7 — secondary residual dispersion aureoles; 8 — superimposed dispersion

specting for mineral deposits is being carried out by locating their supergene lithochemical dispersion flows (in mountainous country) or residual dispersion aureoles (throughout the area), then by pinpointing their primary halos. If lithochemical prospecting is being efficiently used, the hydrochemical and atmochemical methods may be applied on a minor scale, and the biogeochemical techniques should hardly be employed. When type II covered regions are involved, it is possible to prospect for hidden ore deposits in a folded foundation, and for some other mineral deposits in the sedimentary cover, notably, leakage-induced and placer deposits by conducting terrestrial surveys aimed at discovering their secondary superimposed salt and gaseous dispersion aureoles cropping out at the surface of the cover. An alternative technique is to direct exploratory effort to greater depths. This can be achieved through the joint use of litho-, atmo-, sometimes hydrochemical and—in arid regions—biogeochemical surveys. In type III regions the atmochemical method of prospecting

for oil and gas fields is the best, the other techniques of geochemical exploration being given less attention.

The general principle followed in geochemical exploration is to proceed from small-scale surveys of large areas to large-scale surveys of individual districts by linking up these operations to the particular stage of the entire geological prospecting work. In this country each of the stages of this work uses a definite scale, one of geochemical survey techniques playing the principal role (Table 22).
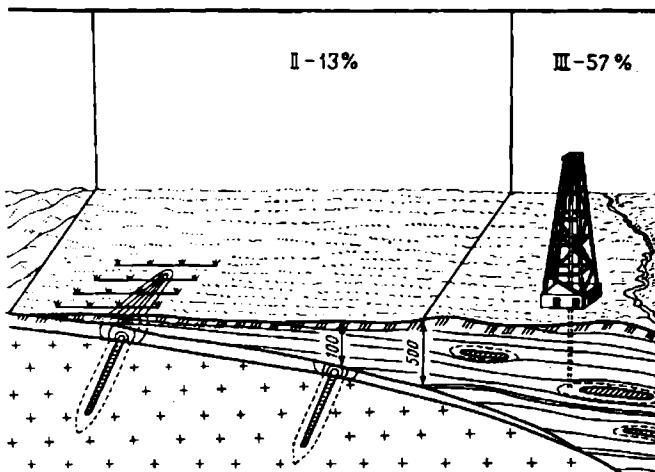
specting:
4 — sedimentary cover; 5 — folded foundation rocks; 6 — orebodies and associated[primary aureoles; 9 — lithochemical (a) and biogeochemical (b) sampling points; 10 — lithochemical surveys profiles

The entire territory of the USSR has by now been covered by national geological surveys on a 1/1 000 000 scale. Regional surveys are now being conducted mainly on 1/200 000 and 1/50 000 scales. 1/1 000 000 and rarely used 1/500 000 and 1/100 000 scales that are adjacent to the principal ones are included in Tables 22-24 for conventional reasons. The above types of geochemical surveys are intended for locating mineral deposits which does not rule out whatever small-scale geochemical surveys for regional mapping, particularly, hydrohelium, litho-, hydro- or atmochemical surveys for environmental protection, for metallogenic or agrochemical and other specific purposes in mind.

Sec. 6.2. Prospecting for Solid-State Mineral Deposits

The current methods of geochemical exploration have in fact emerged during these last fifty years following geochemical prospecting work done in ore-bearing regions, generally to discover and estimate

TABLE 22

Sequence and Possible Combinations of Different Types of Geochemical Surveys

Type of Survey	Scales of surveys and areas surveyed, km²							
	1/1 000 000 and smaller	1/500 000	1/200 000	1/100 000	1/50 000	1/25 000	1/10 000	1/5 000 and larger
	$n \cdot 10^6 - n \cdot 10^5$	$n \cdot 10^4$	$n \cdot 10^5$	$n \cdot 10^4$	$n \cdot 10^4$	$n \cdot 10^2$	$n \cdot 10^2$	$n \cdot 10 - n$
Solid mineral deposits								
Aerial geochemical	+	+	+	+	+	+	—	—
Lithochemical:								
dispersion flows	$+(\pm)$	$+(\pm)$	++	++	$(\pm)++$	$+(\pm)$	$+(\pm)$	$+(\pm)$
secondary aureoles	$-(\pm)$	$-(\pm)$	++	++	++	++	++	++
primary halos	—	—	—	—	—	—	—	—
Hydrochemical	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$
Atmochemical*	—	—	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	—	—
Biogeochemical*	—	—	—	—	—	—	—	—
Oil and gas fields								
Aerial geochemical	+	++	++	++	++	+	—	—
Atmochemical	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	—	—
Hydrochemical	—	—	++	++	++	++	—	—
Lithochemical	—	—	++	++	++	++	—	—
Biogeochemical	—	—	$(\pm)$	$(\pm)$	$(\pm)$	$(\pm)$	—	—

Notations: + + — principal type of operations; + — auxiliary type of operations; (+) — operations of limited value; dash — survey operations are not carried out.

* In covered regions

deposits of nonferrous, rare metals and gold. The general principles, requirements to be met in the evaluation of the discovered anomalies and other conditions of prospecting work hold good for geochemical exploration to locate non-metalliferous deposits, such as phosphorites, boron, asbestos, bauxites, graphite, diamonds, mica, sulphur, rough piezooptical material.

Early stages of exploratory work invariably involve complex operations embracing large areas which fact permits the deposits of different minerals to be expected at the same site. The method of geochemical survey much more depends on the properties of the mineral in hand, whatever the genetic type of the deposit which is revealed at the stages of detailed and evaluation operations.

The term geochemical prospecting should be specified. Prospecting implies any types of survey undertaken to find previously unknown target areas. When doing prospecting work, survey grids are calculated from Eqs. (25)-(26) related to the probability of pinpointing mineralized ground. Once the target of prospecting has been discovered, geochemical surveys that follow are no longer exploratory ones. Observation points in these are more crowded, and their objective is the detailed study and evaluation of the deposit, and, at a definite stage, best siting of mine workings and reconnaissance boreholes. Under such conditions the contour of the geochemical anomaly which provides a guide to a target may contain many tens and even hundreds of observation points the number of which is governed by the morphology and mode of occurrence of the useful component, by the complexity of the geochemical field to be interpreted in quantitative terms and the experience of the prospectors. It would be wrong to object to the choice of the survey net from the standpoint of probability to discover the target in mind. Detailed appraisal surveys

TABLE 23

Dispersion Flow Surveys

Scale	Formal conditions		Lithochemical		Hydro-chemical
	Grid, km	Density, samples per km²	Grid, km	Density, samples per km²	Average density, samples per km²
1 : 1 000 000	10×10	0.01	10×1	0.1	0.05
1 : 500 000	5×5	0.04	5×1	0.2	0.1
1 : 200 000	2×2	0.25	2×0.5	1	0.15
1 : 100 000	1×1	1	1×0.5	2	0.6
1 : 50 000	0.5×0.5	4	0.5×0.25	8	1.7
1 : 25 000	0.25×0.25	16	—	—	3.4

may include surveys on any (not adjacent!) larger scale. At the same time, a survey, whatever its detail, up to a 1/10 000 or larger scale, may be regarded as a prospecting survey with respect to minor and hidden targets the probability of discovering which is to be determined by using the same relationships.

The vast experience available has made it possible to work out concrete requirements to be met by surveying nets and density of observation points depending on what geochemical method is better in the given case (Tables 23-25).

TABLE 24

Secondary Dispersion Aureoles Surveys

Scale	Lithochemical (biogeochemical)		Atmochemical		Hydrochemical	
	Grid, m	Density, samples per km²	Grid, m	Samples per km²	Minimal density, conditions:	
					simple	complex
1 : 1 000 000	10 000×500-200	0.2-0.5	—	—	—	—
1 : 500 000	5 000×500-200	0.4-1.0	—	—	—	—
1 : 200 000	2 000×200	2.5	2 000×100	5	0.1	0.2-0.4
1 : 100 000	1 000×200-100	5-10	1 000×100	10	0.5	1.0
1 : 50 000	500×50-100	40-20	500×100-50	20-40	1.1	1.5-2
1 : 25 000	250×40-50	100-80	250×50-100	80-40	2.3	4-5

TABLE 25

Detailed Lithochemical Surveys

Scale	Secondary dispersion aureole		Primary halo	
	Grid, m	Density, samples per km²	Grid, m	Density, samples per km²
1 : 10 000	100×20-25	500-400	100×50-25	200-400
1 : 5 000	50×10-20	2 000-1 000	50×25-10	800-2 000
1 : 2 000	25×10	4 000	*	High

* Primary halo surveys on 1/2 000 and larger scales involve continuous sampling depending on available test pits underground mines and prospecting boreholes.

No purpose would be served if we compared costs of different geo-
chemical operations on the same scale unless we take into account the
results obtained. It is apparent that dispersion flow geochemical
surveys on a 1/50 000 scale could not substitute more costly litho-
chemical surveys on the same scale referred to secondary dispersion
aureoles which yield geological data of an essentially different char-
acter. The same is true of atmochemical surveys which are conducted
only in covered areas with the thickness of overburden up to 100-
200 m.

What follows presents concrete results of exploratory and more
detailed geochemical surveys viewed in terms of the adopted se-
quence of operations. Case histories of exploration and appraisal for
different geological settings and different minerals make possible
the selection of surveying techniques.

Sec. 6.2.1. Exploratory Surveys

Figure 96 presents results of small-scale hydrochemical surveys
conducted in the southeastern part of the Siberian Platform [14].
Two versions of surveys were used: (1) by sampling surface waters
(observation density—1 sample per 300 km^2; scale—about 1 : 1 500 000);
(2) by sampling subsurface waters (observation density—1 sample per
50 km^2; scale—1 : 700 000). More than 40 thousand km^2 has been
covered. The geology of the region consists of a horizontally bedded
mass of Cambrian-Ordovician carbonate and sandy-aleurolite rocks
with gypsum bands and saliferous at places. The latter circumstance
can be distinctly seen in the map showing the total salt contents of
the surface waters (see Fig 96b) that vary in the range from 0.1 to
24 g/l. Concurrently anomalous high concentrations are manifested
by Cl$^-$ and SO$_4^{2-}$ ions which provides still another proof of hydrochem-
ical prospecting for mineral salt deposits. Very instructive evi-
dence has been obtained by determinations of the trace element con-
tents, including phosphorus and many metals, in the waters. Figure
96c and e, and, respectively, d and f, represent maps of the Ag and
Cu content for the two versions of the hydrochemical survey. In
either case very intense Ag and Cu anomalies have been discovered
that are worth to be studied in more detail. However, the hydrochem-
ical anomalies established by different types of survey are not in
mutual agreement which fact is not accounted for by the authors.
Regretfully, lithochemical samples were not collected during these
surveys.

Figure 97 shows a fragment of a map prepared from the results of
a 1/200 000 scale lithochemical survey of an ore district. The map
demonstrates the contents of two chemical elements, Au and As,
although in actual practice it is customary to prepare single-element
tracing paper maps that are convenient for quantitative interpreta-
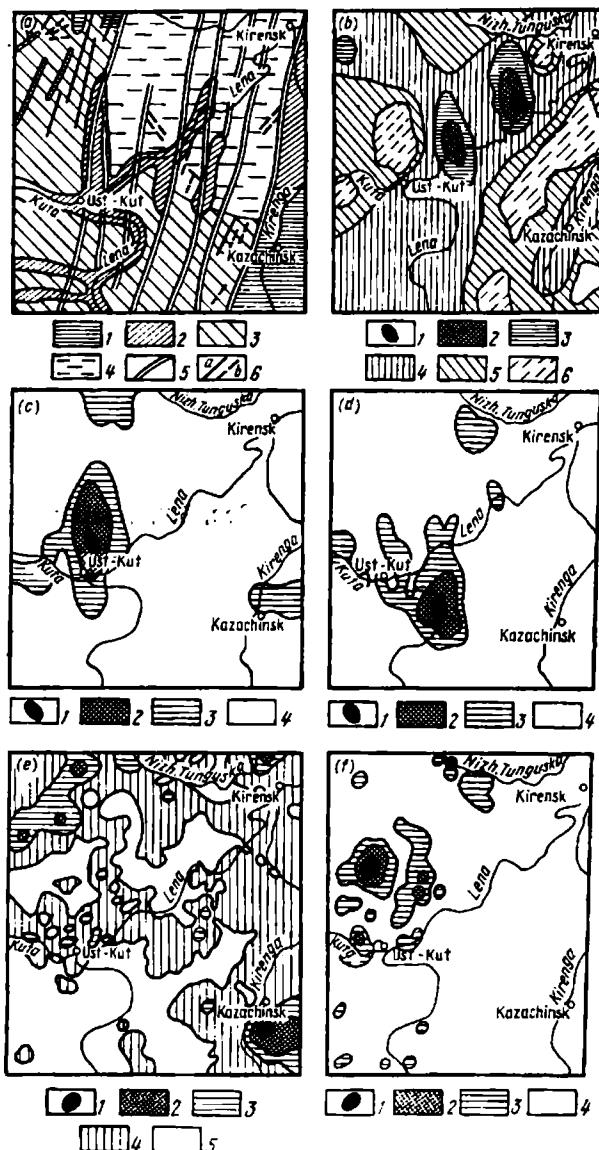
FIG. 96. Hydrochemical maps of the south-east of the Siberian platform. After
I.S. Lomonosov et al:

a — geological setting: 1 — carbonate, saliferous at places, deposits ε_1-ε_2; 2 — marls and
aleurolites with intercalations of sands and gypsum ε_2-ε_3; 3 — sandstones and dolomites
with argillite and aleurolite bands O_1-O_2; 4 — aleurolites and argillites with sandstone
and limestone bands O_2-O_3; 5 — axes of anticlines; 6 — faults determined (*a*) and hypo-
thetical (*b*). *Surface waters,* sampling density 1 point per 300 km²: *b* — total mineraliza-
tion (in g/l): 1—15-24; 2—3.5-15; 3—0.8-3.5; 4—0.2-0.8; 5—0.1-0.2; 6 — less than
0.1; *c* — Ag (in μg/l): 1—19-33; 2—3.5-19; 3—0.4-3.5; 4 — less than 0.4; *d* — Cu (in
μg/l): 1—1.6-2.2; 2—0.6-1.6; 3—0.15-0.6; 4 — less than 0.15 *Subsurface waters,*
sampling density 1 point per 50 km²; *e* — Ag (in μg/l): 1—8-22; 2—2.5-8; 3—0.5-2.5;
4—0.07-0.5; 5 — less than 0.07; *f* — Cu (in μg/l): 1—0.8-1.6; 2—0.3-0.8; 3—0.15-0.3;
4 — less than 0.15

tion and comparison. The district, a part of which is delineated in Fig. 97, features rugged topography with absolute elevations 1 300 to 1 800 m. In terms of landscape the district may be referred to a
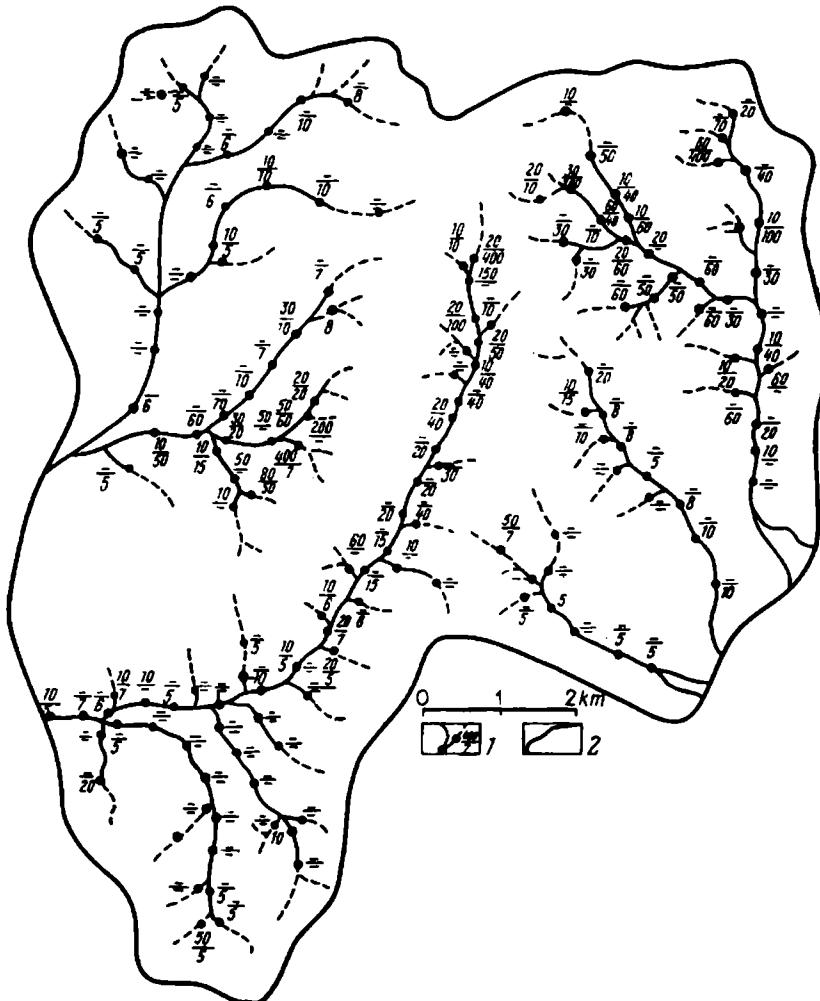
FIG. 97. Results of a 1/200 000 scale lithochemical survey in a mountainous area (fragment). After V.A. Kononov:

1 — sampling points: numerator shows Au content (in 10^{-7} %), denominator shows As content (in 10^{-3} %), dash for Au means less than 10; for As less than 5; *2* — drainage basin contour

permafrost tundra zone; its geology includes Upper Paleozoic sandy-schist sediments with granitoid intrusions. The geochemical map distinctly shows horizontal zoning of the mineralization expressed

16*
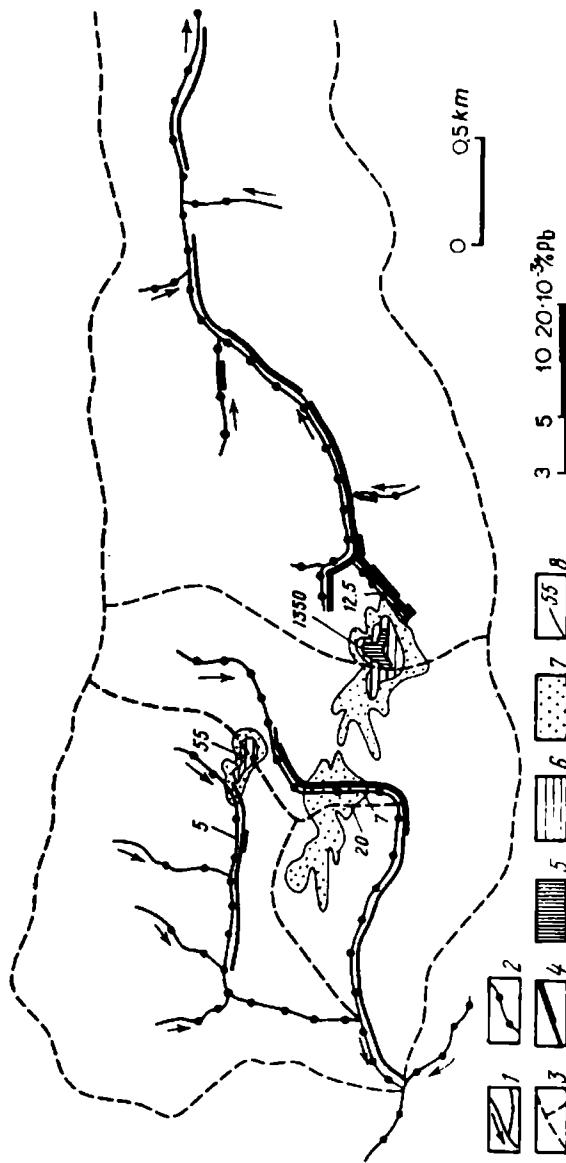
FIG. 98. Secondary Pb dispersion aureoles and flows. Tykzhol district, Dzhungarian Alatau. After S.A. Milyaev:

1 — sampled stream beds and direction of runoff; *2* — sampling points; *3* — watersheds; *4* — dispersion flows; *5-7* — secondary dispersion aureoles (in %): *5* — 0.2-0.5; *6* — 0.05-0.2; *7* — 0.005-0.05; *8* — maximum Pb contents in dispersion aureoles and flows (in 10^{-3} %)

by a change of predominantly auriferous dispersion flows by Au-As flows in the western part of the district, and by As dispersion flows in the northeastern part. Quantitative analysis of these and adjacent Au and As dispersion flows has enabled the reserves of the district to be estimated and a decision as to its further study to be made. The results of a 1/50 000 scale lithochemical survey have validated this estimate.

Dispersion flow lithochemical surveys with an observation density of 1 sample per km² (spacing 2 × 0.5 km) are being regularly conducted in the northeastern regions of the USSR and have proven effective.

An example of joint results of a dispersion flow (spacing 100 m) and a secondary dispersion aureole lithochemical survey on a 1/10 000 scale of the Tykzhol district (Fig. 98) shows the obtained data are in full agreement in quantitative terms. The results of these surveys made it possible to evaluate the local values of the proportionality coefficients k' between the productivities of the dispersion flows and dispersion aureoles in conformity with

FIG. 99. Areal exploratory geochemical surveys in an ore district during a number of years:

1 — recent sediments; 2—200 m isopachous contour line; 3 — ore bearing rock mass; 4 — mineralized zone; 5-7 — terrestrial lithochemical surveys on 1/50 000 scale of 1983 (5), of 1984 (6); planned (7); 8 — planned atmochemical survey on 1/100 000 scale

Eqs. (16) and (35). Some of the mean values of k' for principal ore elements for the Jungar Alatau are presented in Table 11.

Regular surveys on a 1/50 000 and adjacent scales are the most important type of geochemical exploration in orebearing regions. When an uncovered region is involved, these surveys use the lithochemical method of prospecting for deposits by locating their secondary residual dispersion aureoles in eluvio-deluvium of recent origin. These lithochemical or "metallometric" surveys are highly efficient, whatever the landscape zone. It is owing to these surveys that since 1935 a number of economically important deposits have been discovered in the USSR. Prospecting for major hidden deposits by pinpointing their superimposed dispersion aureoles may be continued in covered regions with the overburden of 100 to 120 m. Under such conditions they should be combined with terrestrial atmochemical surveys alternated by sporadic deep lithochemical surveys on a 1/100 000 scale.

All types of surveys should use relevant trapezoid sheets without any arbitrary omissions so as to fit into the long-term survey plans (Fig. 99). An example of the discovery by 1/50 000 scale lithochemical

surveys of a tin ore deposit in the Maritime Region is presented in Fig. 100. The deposit was omitted during a heavy concentrate panning survey which had located other tin ore deposits in the same district. This is attributable to insufficient erosion of the given deposit which is amply evidenced by the fact that Pb dispersion aureoles distinctly dominate Sn aureoles. Similarly to other tin ore zones, in the particular case Pb plays the role of a supraore element (cf. Fig. 79).

The success of geochemical exploratory surveys depends on how accurately the discovered anomalies are appraised in which step a number of essential requirements should be satisfied. The most important of these is a geological field observation of the anomalies followed by repeated control and detailed surveys by using the same method as the one that has discovered the anomaly in question. This requirement is valid for early estimates of litho-, hydro-, atmo- or biogeochemical anomalies the availability of which should be substantiated by similar repeated surveys before proceeding to other types of work. Handling by office work of the data obtained makes it possible to determine the priority of anomalies; it is impermissible to discard an anomaly without a geological field observation. The principles of the evaluation of supergene lithochemical anomalies have been elaborated the best and can, after some corrections, be used when other methods are involved.

Supergene anomalies that can be detected by lithochemical surveys fall into three principal classes. The first includes *ore anomalies*, i.e. secondary dispersion aureoles and dispersion flows associated with primary ore; the second class includes *barren anomalies* which, in turn, should be divided into rock anomalies referred to rock with increased clarke values of ore elements, and supergene concentrations of ore elements at geochemical barriers. The third class includes *technogenic* lithochemical anomalies referred to the cultured stratum. During exploratory work natural barren and technogenic anomalies should be discarded and their lithologopetrographic characteristic, type of the geochemical barrier or origin should be specified.

Similar requirements should be met by a geological observation and quantitative analysis of dispersion flows and exposed at the modern ground surface of secondary dispersion aureoles main types of which were presented in Fig. 28 when the class of ore lithochemical anomalies is involved. In this case, superimposed and concealed dispersion aureoles, including partially hidden aureoles should be studied by deep lithochemical surveys followed by the appraisal of reserves from parameters of residual dispersion aureoles. It is the objective of the appraisal of supergene ore anomalies to determine the genetic type and possible economic importance of the associated mineralization expressed in the values of expected reserves of metal. The final step is to decide as to the plausibility and priority of a more detailed study of the discovered targets of search. The relevant
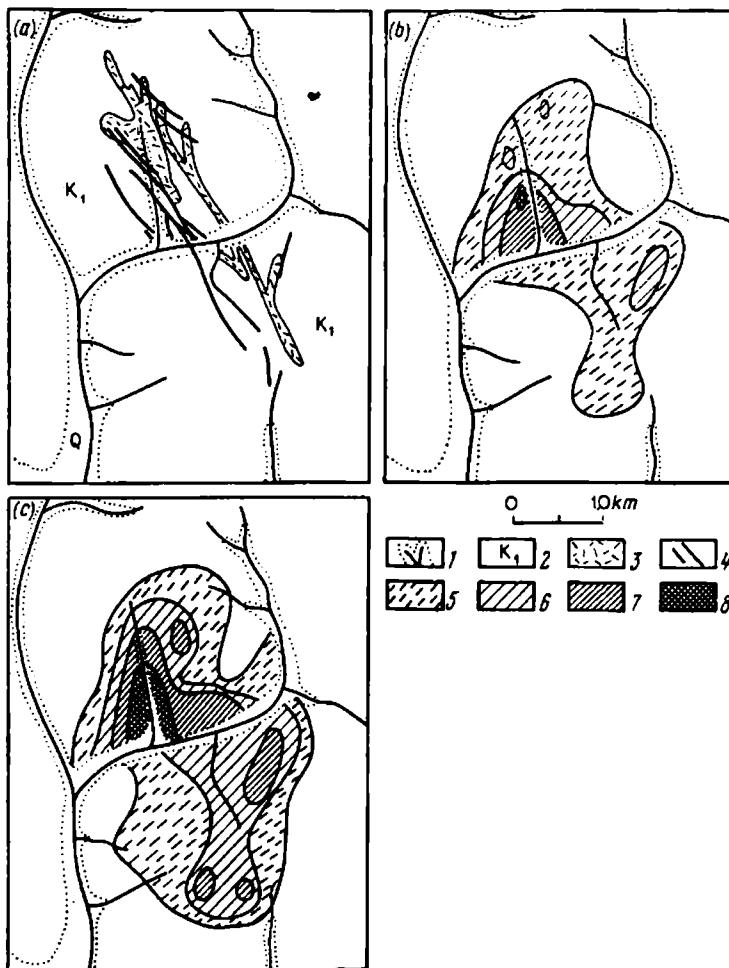
FIG. 100. Geological setting (a) and secondary dispersion aureole of Sn (b) and Pb (c) from the results of lithochemical survey on 1/50 000 scale in the Maritime Region. After P.A. Kurshev:

1 — alluvial sediments; *2* — Lower Cretaceous sandstones and aleurolites; *3* — quartz porphyry dykes and subvolcanic bodies; *4* — ore veins; *5-8* — metal contents in eluvio-diluvium (in 10^{-3} %); *5* — Sn 1-2; Pb 3-6; *6* — Sn 2-6, Pb 6-20^{-4}; *7* — Sn 6-20, Pb 20-60; *8* — Sn 20-60, Pb 60-200

estimates are validated by detailed, repeated control and ore lump sampling, geological diagrams and detailed calculations.

If a target is estimated to be associated with a large or medium-size deposit, priority is given to operations of the next stage. Targets assumed to be associated with small deposits are studied next,
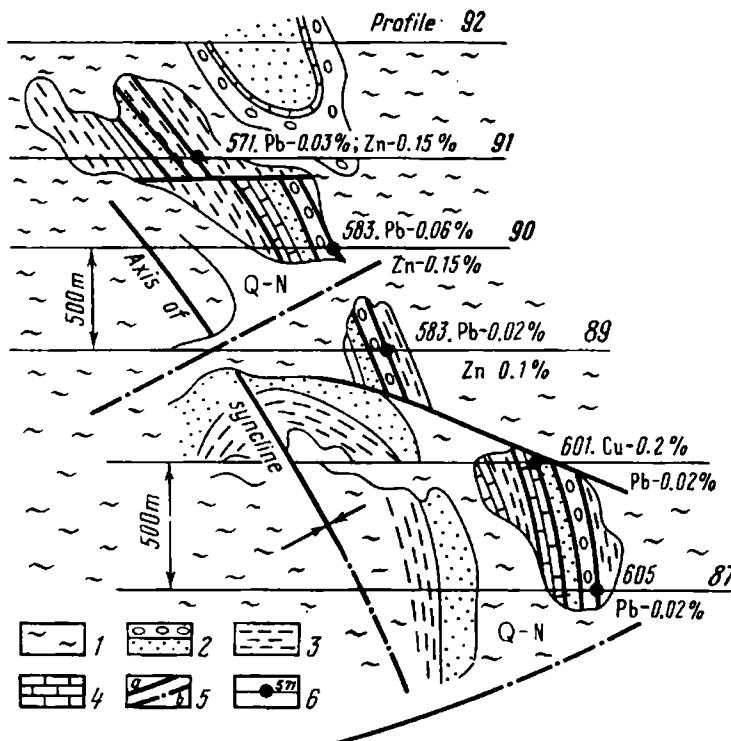
FIG. 101. Geological setting determined from results of the inspection of the anomaly and aerial photograph interpretation. After L.M. Filinskii:

1 — Neogene-Quaternary sediments; 2 — gravelly conglomerates (circles) and gravellites (points); 3 — aleurolites and aleurosandstones; 4 — limestones; 5 — tectonic disturbances (a — detected, b — hypothetical); 6 — stations of lithochemical survey on 1/50 000 scale showing anomalous metal contents

mineralizations of noneconomic importance are discarded following from the results of a geological observation. Geological interpretation will be more adequate if field records of sampling operations rely on aerial photographs. Before these latter are interpreted in the field, anomalous high contents of ore elements are shown in the photographs. This is illustrated by Fig. 101. A lithochemical survey on a 1/50 000 scale, followed by a detailed 1/10 000 scale survey and by mining and drilling operations has discovered a stratiform polymetallic

deposit estimated to be of a medium size. The mineralized area is located in the arid steppe zone with smooth relief and is inappreciably exposed. The residual Pb dispersion aureoles are decayed (k is less than 1.0).

We should distinguish between the principal morphological types of secondary dispersion aureoles revealed by geochemical prospecting of ore-bearing districts (Fig. 102). In mountainous "uncovered" parts the lithochemical method is used for prospecting, type A and B
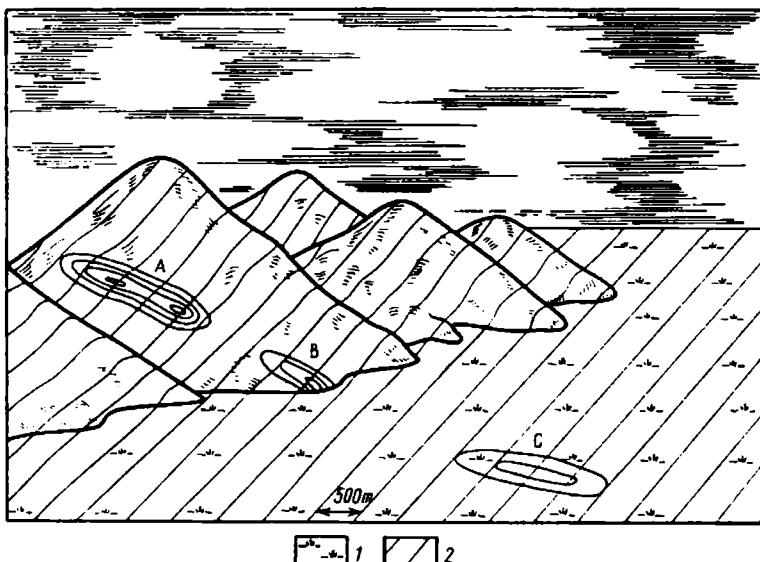
FIG. 102. Morphogenetic types of secondary dispersion aureoles: A — residual (eluvio-deluvial), completely exposed; B — residual, partially concealed; C — superimposed; 1 — piedmont valley; 2 — lithochemical survey profiles

dispersion aureoles being residual ones. In a piedmont covered part of the district blanketed by a cover of allochthonous sediments, terrestrial surveys reveal superimposed (type C) dispersion aureoles which in particular may involve lithochemical, atmochemical, including gaseous mercury or biogeochemical, techniques.

In regions with expected ore that have been poorly investigated where lithochemical surveys are first conducted, it is a good plan to direct exploratory effort toward the discovery of vast and intense residual dispersion aureoles of type A which is evidenced by actual important discoveries. When mineralization belts that are relatively well studied in geological and geochemical terms are involved one is hardly likely to discover a new major deposit of economic ore exposed

to the ground surface by locating an intense and extended residual dispersion aureole. We are more likely to discover new targets at an early erosion stage by pinpointing relatively impoverished supraore aureoles (type A) or ones that are found in unfavourable geomorphological environment (type B). That is why it is necessary to reappraise discovered weak lithochemical anomalies that failed at first to attract our attention. We must also take into consideration the well-known fact that the total number of supergene lithochemical anomalies to be found in uncovered mineralized regions exceeds by a large margin that of economically important deposits.

To locate hidden deposits in covered regions is a paramount problem faced by economic geology. Such regions include ones to be found in the Voronezh anteclise area where 200 thousand km^2 of a crystalline foundation is overlain by a sedimented cover not more than 200 m in thickness; more than 600 thousand km^2 in Kazakhstan with the same sedimentary cover; the Ukrainian crystalline massif with the same thickness of overburden; Siberian trap regions and other possible mineralized regions totalling about 3 million km^2 in area.

The established possibility to locate, in principle, hidden ore deposits by atmochemical techniques aimed at discovering aureoles of a complex of indicator gases enabled trial industrial scale surveys on a 1/100 000 scale to be undertaken in covered regions of Kazakhstan with an objective to elaborate the procedures and techniques for these surveys. Figure 103 presents the results of such a survey encompassing an area of 500 km^2 in the eastern flank of the Turgai depression. The folded foundation of this district is composed by Paleozoic and Pre-Cambrian rocks, the cover 10 to 100 m in thickness is composed by sandy clay sediments of the Paleogene-Quaternary period. The region refers to the arid steppe zone. Atmochemical surveys used a sampling grid 1000 × 100 m involving gas samples collected from 3.0 m deep auger holes. Concurrently a terrestrial lithochemical survey on a 1/50 000 scale was conducted of this area with sampling depth 0.3 m followed by spectral analysis, multiplication and smoothing of the ore element contents.

The atmochemical survey discovered 14 extended gaseous anomalies formed by various combinations of anomalous contents of carbon dioxide, methane, hydrogen and oxygen, a fraction of these agree with multiplicative lithochemical aureoles (see Fig. 103). The maximum contents were (in %) here as follows: CO_2—3.6, background being 0.2; CH_4—530 × 10^{-4} with background 1.5 × 10^{-4}; H_2—350 × 10^{-4} with background 2 × 10^{-4}; the minimum O_2 content is 18.2 with background being 20.2. Testing gaseous anomalies by deep lithochemical surveys (Fig. 104) followed by core drilling led to a discovery of two stratiform polymetallic ore showings called Alys and Arykbaksy. Most gaseous anomalies later proved to be guides to ore. Although the economical importance of these deposits

has not as yet been determined, the results obtained attest to the first discovery of a concealed mineralization from the data of an atmochemical survey.

That it is feasible to discover superimposed lithochemical dispersion aureoles above concealed polymetallic metal deposits was proved
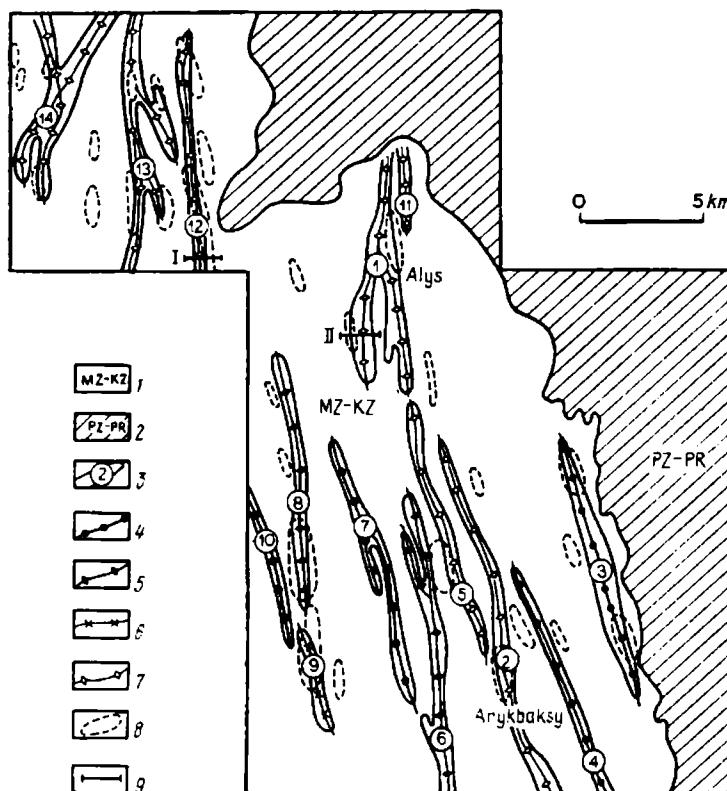
FIG. 103. Results of a 1/100 000 scale atmochemical survey. Turgai depression. After B.A. Dosanova, V.N. Kolesnikov, S.A. Vorob'ev:

1 — Mesozoic and Cenozoic sediments; *2* — Paleozoic and Pre-Cambrian rocks; *3* — contours of coincident gaseous anomalies and their sequence numbers; *4-7* — axes of gaseous anomalies: *4* — CH_1, H_2; *5* — CO_2, CH_1, H_2; *6* — CO_2, H_2; *7* — CO_2, CH_1, H_2, O_2; *8* — superimposed lithochemical multiplicative dispersion aureoles (Pb, Ag, Hg, Co); *9* — deep lithochemical survey profile

in the Rubtsovskii district in the Rudny Altai. Ore enclosing effusive sedimentary Paleozoic rocks submerge here under a cover of Meso- and Cainozoic sediments the thickness of which at the area investigated is 100-120 m. The ore deposits of this mineralized zone refer to the well-known pyrite-polymetallic formation of the

Altai type with massive sulfides ore deposits most advantageous for
the origination of superimposed salt dispersion aureoles. In terms
of landscapes the district refers to the zone of southern Chernozem
steppes with moderate wetting, the most part of the area is used for
crops. Terrestrial lithochemical surveys were conducted on scales
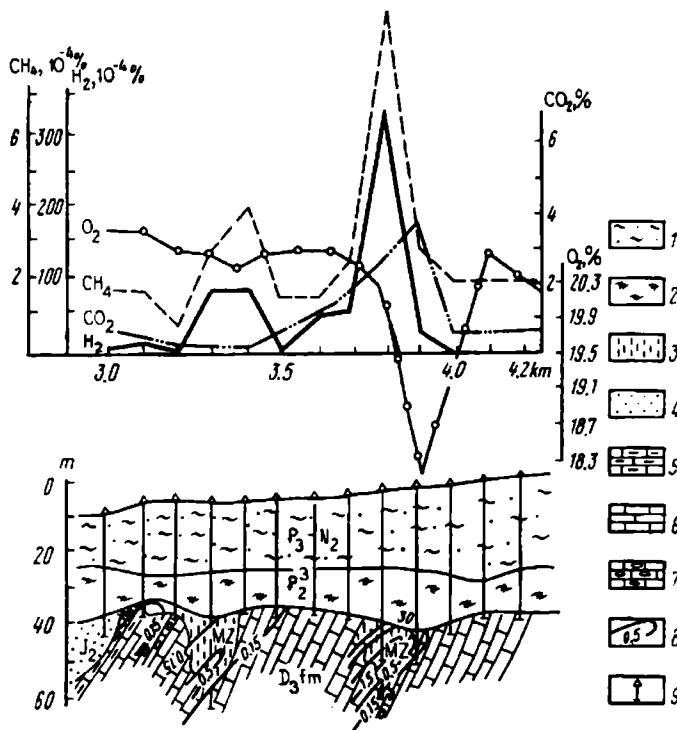
FIG. 104. Graphs of an atmochemical survey and geological section from results
of a deep lithochemical survey of the Alys district. (Profile *II*, see Fig. 103):
1 — sandy-clayey sediments (P_3-N_2); *2* — clays (P_2); *3* — weathering crust (MZ); *4* — sands
(J_2); *5* — coal carbonate shales; *6* — limestones (D_3); *7* — silicified limestones; *8* — Pb iso-
concentration (in %) contour lines; *9* — auger drilling

1/50 000-1/25 000 with sampling depths 20-30 cm. No reliable re-
sults from the initial data referred to the tested areas have been ob-
tained. In order to detect superimposed dispersion aureoles over
known deposits acetate buffer extraction methods were used involving
determinations of the total Cu, Pb, Zn content [28] and bulk spectral
analysis followed by computerized multiplication and smoothing
of Pb, Cu, Zn, Ag, Ba contents. Intense superimposed dispersion au-
reoles were discovered by the two methods over the Talovskoye,
Rubtsovskoe and Kryuchkovskoe concealed polymetallic de-

posits. In this region later reconnaissance surveys were conducted
by the second, simpler and more economical method covering an
area more than 2000 km². This handling of initial data enabled a
number of lithochemical anomalies of different origin to be discov-
eed. Deep lithochemical surveys and core drilling have proved that
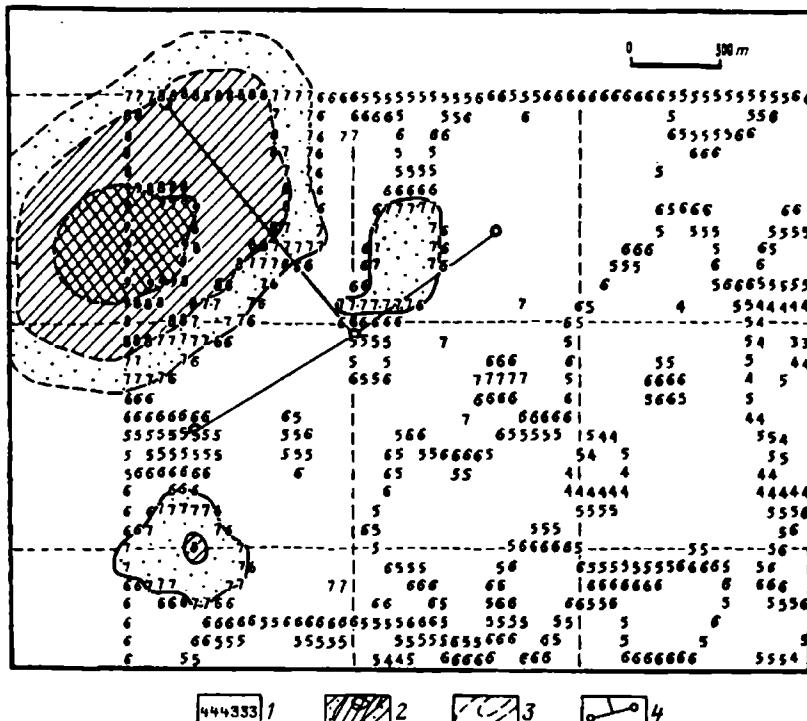
FIG. 105. Fragment of listing of computerized data processing ¦of a 1/25 000
scale terrestrial lithochemical survey. Data submitted by I.F. Myasnikov,
processed by Moscow State University:

1 — value of index $I_3 = \dfrac{Pb \cdot Zn \cdot Cu \cdot Ag \cdot Ba}{Mo \cdot B}$; 2 — established lithochemical anomalies; 3 —
anomaly contour; 4 — deep lithochemical survey profiles substantiating ore origin of anom-
aly

most of these anomalies refer to superimposed aureoles of a concealed
mineralization. Concurrently, a group of barren anomalies have been
pinpointed that originated through the supergene accumulation of
ore elements in local landscapes. In order to suppress barren anoma-
lies an empirical coefficient $I_2 = \dfrac{Pb \cdot Cu \cdot Zn \cdot Ag \cdot Ba}{B \cdot Mo}$ has been pro-
posed. An example of superimposed dispersion aureoles at the Po-
teryaevskii ore district is given in Fig. 105 as a computer listing.

That the anomaly that failed to be exposed at the ground surface in any way provides a guide to ore has been manifested by deep lithochemical surveys. Referred to two profiles across the anomalies the zinc content was found to be up to 0.2%, the copper content up to 0.15%, lead content up to 0.08%. Of 21 exploratory boreholes, 17 showed anomalous ore element contents. The thickness of the overburden composed by allochthonous sediments in this district is 80-90 m. It seems quite reasonable to continue operations at this target of search.

Deep lithochemical surveys provide the most reliable method of geochemical exploration of covered areas if on the surface of the foun-
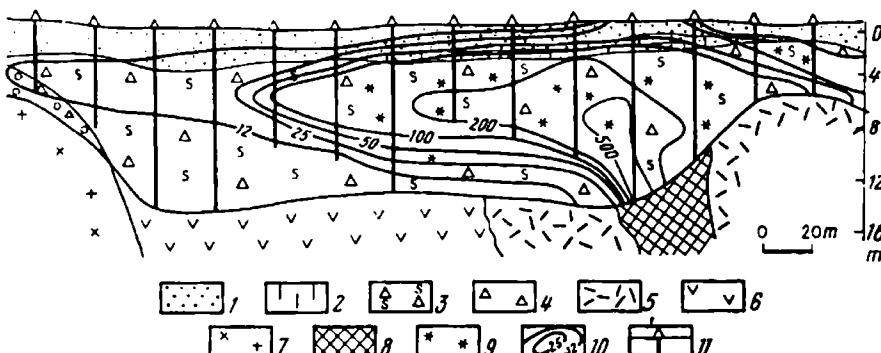
FIG. 106. Concealed Cu dispersion aureoles from the results of a deep lithochemical survey. After V.A. Bugrov:

1 — allochthonous sediments; ancient weathering crust horizons; *2* — bleached clayey; *3* — clayey crushed rock; *4* — crushed rock; *5* — albitophyres; *6* — basic composition effusive rocks; *7* — granodiorites; *8* — limonites; *9* — ochrization and jarozitation; *10* — Cu isoconcentration (10 %) contour lines; *11* — auger drilling boreholes

dation takes place the ancient-origin crust of weathering. It is possible to locate deposits of any genetic type and scope of mineralization, whatever the thickness of overburden, and present-day landscape conditions which are of the most importance for the origination of superimposed dispersion aureoles.

High costs of deep lithochemical surveys which increase with the thickness of the allochthonous sediments are the main factor preventing their extensive use. That is why in modern practice these surveys use a method of profiles in order to test geochemical anomalies discovered by terrestrial atmochemical, lithochemical or biogeochemical surveys on the surface layers of the sediment cover. After these anomalies have been proved to be guides to ore, deep lithochemical surveys of a limited area are conducted on a 1/25 000 scale using a rectangular grid so as to possibly remain within the contour of the residual dispersion aureole. Concealed dispersion aureoles should be extensively studied involving redrilling and sampling of the entire

profile of the crust of weathering. Referring to these data, large-scale horizon-by-horizon geochemical plans and cross sections are plotted in isoconcentration values as shown in Fig. 106 and previously in Figs. 29, 40. From the parameters of the concealed residual dispersion aureoles prospective metal reserves are calculated to decide whether it is plausible and expedient to drill deeper prospecting boreholes.
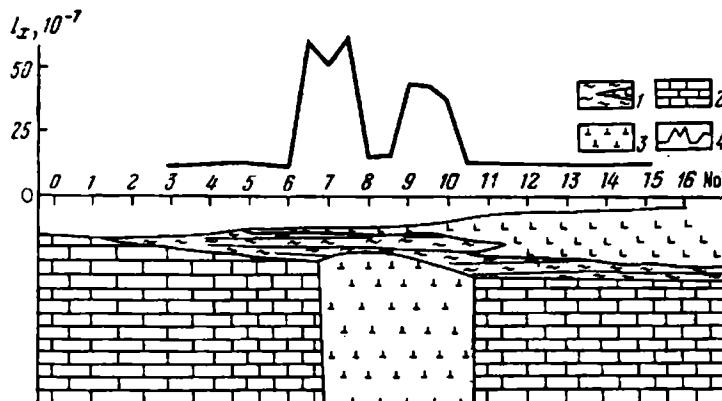
FIG. 107. Results of terrestrial lithochemical survey over a kimberlite pipe. After S.A. Vorob'ev:

1 — overlying terrigenic sediments and traps C_{2+3}-T_1; 2 — limestones O_2-S_1; 3 — kimberlites; 4 — graph of multiplicative ratio $I_x = \dfrac{Ca \cdot Mg \cdot S \cdot P \cdot Co \cdot Ni}{Al \cdot V \cdot Ga}$

Providing still another illustration of the promise offered by geochemical exploration of covered areas, Fig. 107 presents the results of lithochemical testing of a concealed kimberlite pipe overlain by traps and terrigene sediments. The graph of the multiplicative index $I_x = \dfrac{Ca \cdot Mg \cdot S \cdot P \cdot Co \cdot Ni}{Al \cdot V \cdot Ga}$ chosen by comparing geochemical characteristics of kimberlites, enclosing limestones and overlying deposits displays an anomaly determining the location of the pipe. The numerator of this exploratory geochemical index includes the product of element contents that are in excess in kimberlites compared with the enclosing and overlying rocks; the denominator is made up by elements that are in deficit in kimberlites. Being formally similar to the zoning index v the exploratory index I_x is selected by proceeding from different principles. The dimensionlessness requirement is invalid for it. The two-peaked shape of the graph (see Fig. 107) preserved after smoothing the data with a sliding window $n = 3$ is quite consistent with the concepts of the largest mobility of chemical elements in the pipe contact zone, "inheritance" by overlying sediments of subtrap tectonics and its being mirrored in the supergene geochemical field.

Sec. 6.2.2. Detailed and Evaluation Survey Operations

Whether it is reasonable to undertake detailed survey operations is generally determined from the results of the previous geochemical exploratory surveys and evaluation, in geological terms, of the targets discovered. The results of prospecting operations permit the estimation of prospective reserves of categories P_3 and P_2 and choice of methods of detailed surveys, size of the area, orientation of the survey net and a list of determined elements. Unlike prospecting surveys that can be made by using any geochemical method, detailed surveys mainly use surface or subsurface versions of the lithochemical method usually jointly with geophysical investigations. A 1/10 000 scale terrestrial survey is commonly sufficient for detailed contouring of secondary residual dispersion aureoles associated with polymetallic, lead, copper, tin-ore and most rare-metal deposits and for starting drilling operations. When gold ore, beryllium, cobalt and mercury deposits are involved and in a search for concealed orebodies by locating their secondary dispersion aureoles 1/5 000, less commonly 1/2 000 scale surveys may be used. When conducting deep lithochemical surveys with the objective to delineate and evaluate concealed residual dispersion aureoles, a 1/25 000 scale is generally the one used for final surveys. Blind orebodies are being looked for by their primary halos with any degree of detail governed by the geological setting and available mine workings and boreholes that can be used for sampling.

As we pass from prospecting to detailed lithochemical surveys, the number of individual anomalies increases, their average geometrical size diminishes and configuration becomes more complicated, the maximum ore element contents increasing. In this case, the total areal productivity of anomalies within the given district does not change. However, given a small size of the anomaly and a semicovered district, the consistency in productivity estimates is violated.

This is illustrated by the polymetallic deposit discovered in Kazakhstan. Lithochemical prospecting surveys on a 1/50 000 scale have revealed here fairly vast and rather weak dispersion aureoles with maximum Pb content 0.04-0.07% referred to Upper Devonian carbonate sediments. None of these aureoles drew particular attention. A geological survey on the identical scale of the same district had been shortly conducted that failed, too, to reveal this deposit.

The region in hand features smoothed hilly relief with some denudation and from the viewpoint of landscape belongs to an arid steppe zone with wild wormwood and cereal vegetation. It is only a 1/10 000 scale detailed lithochemical survey that discovered here a local dispersion aureole with the Pb content in eluvio-deluvium 0.6% determined in three adjacent profiles and $C_{max} = 1.25\%$ Pb (Fig. 108) referred to a small isolated hillock composed by silicified

and ferruginated limestones. Exploratory trenches have uncovered here cerussite ores and found out that the ore deposits were submerged in a northwestern direction under a cover of Neogene-Quaternary sediments. Drilling operations that followed attested to the economic importance of this mineralization.
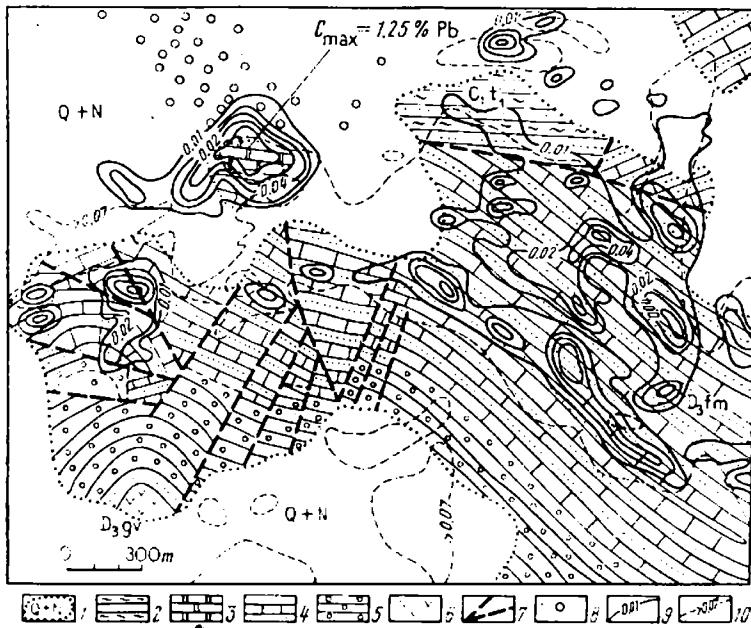
FIG. 108. Results of a detailed 1/10 000 lithochemical survey in the Uzunzhal deposit district. After V.A. Klichnikov:

1:— Neogene-Quaternary deposits and their boundary; *2* — limestones, sandstones and slates of Lower Carboniferous; *3* — enclosing sandstones, dolomites and coaly limestones of Etroeungt; *4* — calcareous sandstones and limestones of Famennian; *5* — conglomerates, sandstones, tuff sandstones of Frasnian; *6* — porphyrites, quartz porphyrys, sandstones of Givetian; *7* — rupture discontinuities; *8* — exploratory boreholes; secondary dispersion aureoles (in %); *9* — Pb; *10* — Zn

The secondary residual dispersion aureoles associated with this deposit is a typical example of partially hidden one (see Fig. 102*b*). Such dispersion aureole cannot characterize the scope of the primary mineralization unless the hidden part of the zone takes place. The thickness of Neogene. Quaternary sediments is 30-40 m. This illustration is only one of the results of prospecting and more detailed lithochemical ("metallometric") surveys that were extensively conducted in Kazakhstan since 1949. Modern arid climate, predominant steppe landscapes, geochemical surveys made jointly with geological and geophysical investigations were what ensured the high efficiency of these operations [13, 20].

Detailed lithochemical surveys and subsequent drilling operations involve accumulation of local coefficients of residual productivity greater or less than unity needed for the adequate appraisal of the discovered dispersion aureoles. For each of the main metals economically important deposits of which are developed in the given district the values of k found from Eqs. (18), (19) or (69) can be best grouped according to the principal geochemical landscape types typical for the area under study. An example of such kind is shown in
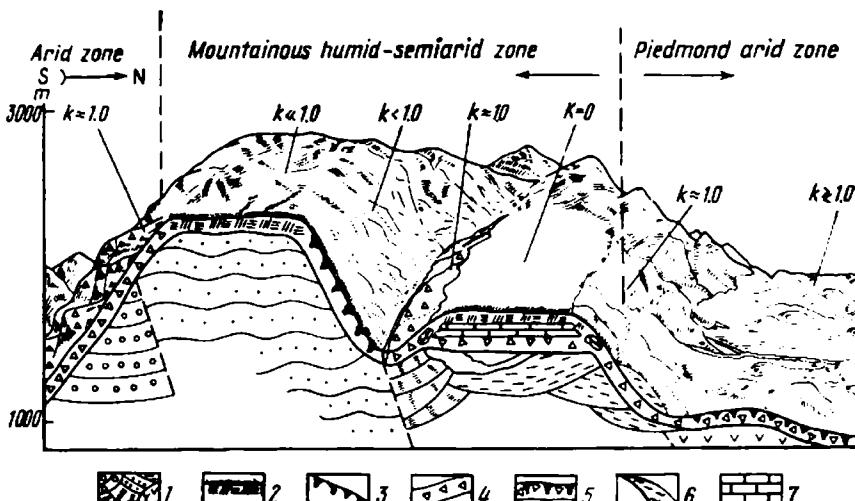
FIG. 109. Diagram of the development of secondary Pb dispersion aureole for the Zailiisky Alatau [20]:

1 — Paleozoic and Pre-Cambrian enclosing rocks; 2 — eluvium of eroded watersheds with mountainous meadow soils; 3 — north exposed slope eluvio-deluvium with well developed soils; 4 — south exposed slope eluvio-deluvium with coarse skeleton crushed rock soils; 5 — eluvio-deluvium of piedmont hillocky areas with dry steppe poorly developed soils; 6 — "leaning" loess-like loams; 7 — Neogene marly limestones

Fig. 109 [20]. Mountainous structures of this ridge are associated with Alpine orogeny and manifest table-type step-like uplifts alternated by deeply eroded steep slopes. Under such conditions coefficients of the residual productivity of secondary dispersion aureoles change dramatically as we pass from smoothed watersheds with absolute elevations about 2 500 m and mountain meadow soils ($k_{Pb} \approx$ 0.07) to intensely eroded south exposed slopes with ill developed clastic soils ($k_{Pb} \approx 1.0$). With decreasing absolute point elevations the differences between the south and north exposed slopes diminish. Of importance is the presence of covered territories in this district — areas of remaining Neogene limestones and modern "leaning" loesses with $k = 0$. The compilation of such reference data is necessary for any orebearing region.

The results of a detailed lithochemical survey on a 1/10 000 scale shown in Fig. 110 are very instructive. Secondary residual Pb dispersion aureoles here are precisely reflecting the scope and mode of occurrence of orebodies of the Tekeli, Dzhungarian Ala Tau, deposit. The significance and multitude of geological conclusions that can be inferred from analysis of the supergene dispersion aureoles is shown in Fig. 111. The Levoberezhnoe ore showing referred to the ore field of the same deposit is associated with carbonate schist rocks of the Tekeli suite and located in two tectonic blocks. The scope of the polymetallic deposit at the ground surface is characterized by secondary Pb dispersion aureoles, additional information being provided by multiplicative Ag·Sb dispersion aureoles (supraore association) and Mo·Cu dispersion aureoles (subore association). The western tectonic block shows very weak Ag·Sb dispersion aureoles and fairly distinct Mo·Cu dispersion aureoles. Intense Ag·Sb dispersion aureoles were discovered within the eastern block in the absolute absence of anomalous Mo and Cu contents. The observed relationships unambiguously point to the deep erosional surface of the western block and probable important mineralization of the eastern block.

The above example illustrates a necessity to pay constant attention to the "geochemical spectra" of the primary mineralization and lithochemical anomalies detected by prospecting work. This term is commonly used to define a graphical representation of the chemical composition of the target of search ordered in a certain fashion and reduced to a form easy for comparing with similar targets [20]. To plot geochemical spectra we select a definite (say, ordered in terms of clarke values) location of ore elements on the abscissa axis, given a logarithmical scale of the representation of their average contents (or productivities) on the ordinate axis. In this case the differences between or similitude of the targets can be determined by shifting one of the graphs along the ordinate axis until they agree with respect to the principal ore, or any other element. This rules out the effect of indices of "impoverishment" or "richness" of the targets being compared.

It is possible to express the differences between two similar prospecting targets by using a dimensionless geochemical index ν the numerator of which is made up by contents of elements that are in excess in target A compared with target B; the denominator containing element contents that are in relative deficit in target A. A measure of difference will then be provided by the value of the ratio ν_{max}/ν_{min}.

It is possible, by referring to numerical values of ν_i, to comparatively evaluate the level of the erosional surface of genetically similar targets. However, in order to more reliably evaluate $\overline{Z}_i$, zoning indices of a standard deposit must be used (cf. Chap. 4). The same

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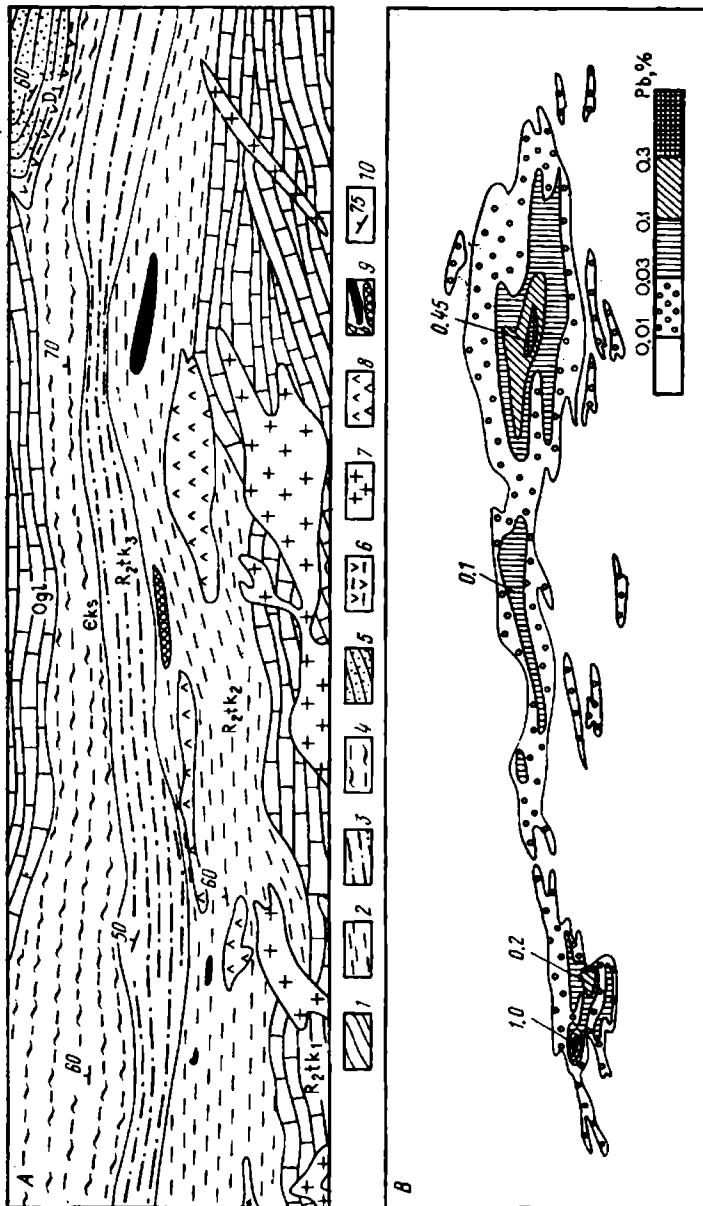
FIG. 110. Geological setting (A) and secondary Pb dispersion aureoles (B) of the Tekeli ore field. After V.E. Flerov and S.A. Milyaev:

1 — subore limestones; 2 — interbedding of limestones, clayey shales; 3 — supraore coal and siliceous shales, coal, coal and clayey shales; 4 — clayey and siliceous shales; 5 — sandstones; 6 — andesite porphyrites; 7 — granite porphyrys; 8 — diabase porphyrites; 9 — orebody outcrops (α) and projection of blind orebodies (b); 10 — elements of occurrence of rocks
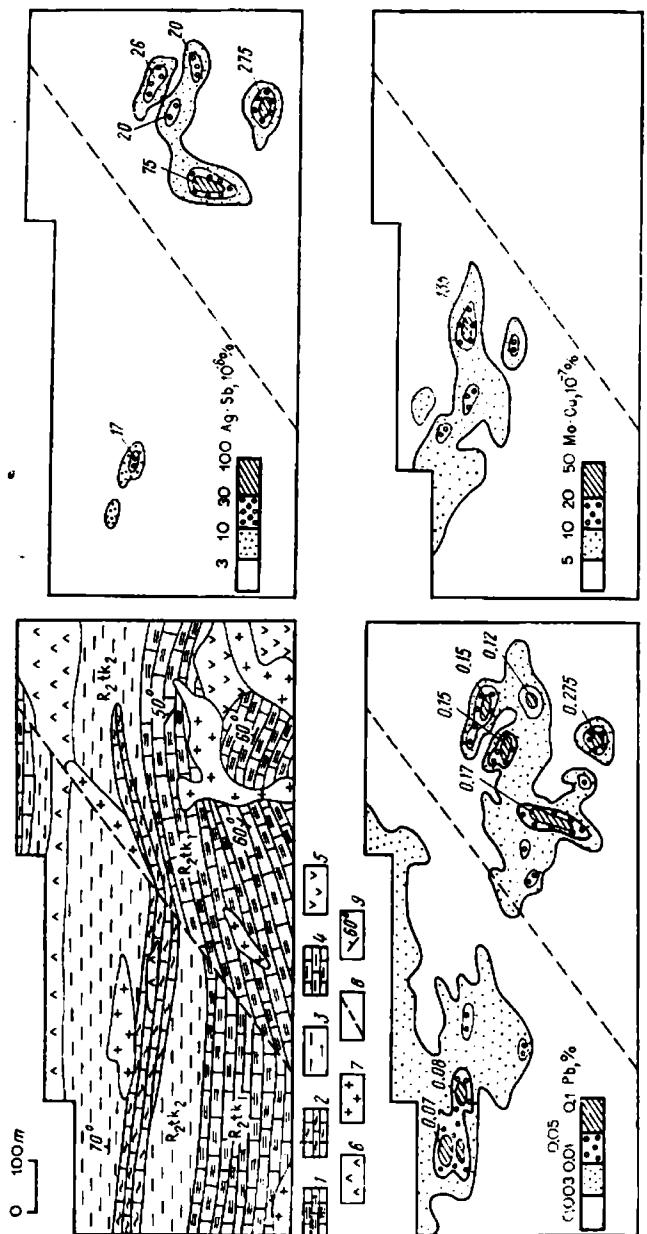
FIG. 111. Geological setting and secondary dispersion aureoles of the Levoberezhnoe complex ore showing. After R.A. Degtyarev and S.A. Milyaev:

1 — limestones, calcareous clay slates intercalations; *2* — clayey limestones; *3* — coal shales; *4* — coal limestones; *5* — andesites; *6* — diabase porphyrites; *7* — granite porphyrys; *8* — tectonic disturbance; *9* — elements of occurrence of rocks

indices are relied upon to determine genesis of targets whose charac-
teristics are close to one another and to infer a similarity in the level
of their erosional surfaces. Since one is unable to resolve two problems
by referring to a single characteristic, to remove ambiguity absolute
contents of the most important ore elements or their productivities
(C_{max}, M_t, P_i) should be taken into account. Similar to linear geo-
chemical spectra, circular spectra (Fig. 112) are plotted. This method
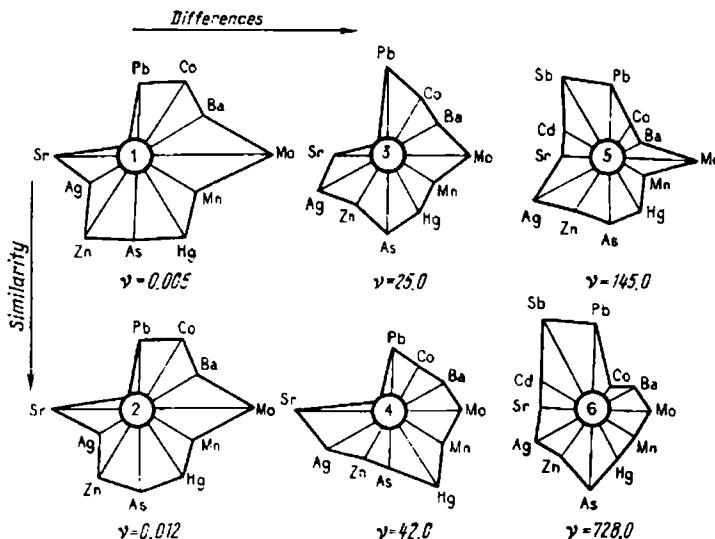
FIG. 112. Circular geochemical spectra of Cu deposits of the Spasskaya mineral-
ized zone. Ratio of average contents of 12 ore elements to Cu contents; circle
diameter equals log 10. After I.A. Kosheleva.
Formations: *1, 2* — Post-Middle Devonian Mo-Cu; *3, 4* — Post-Middle Devonian Cu; 5,
6 — Middle Devonian Cu $v = \dfrac{\text{Pb} \cdot \text{Ag}}{\text{Mo} \cdot \text{Co}}$

allots definite sites on a circle to typomorphic complex elements.
Having been divided by the principal metal content, relative ele-
ment contents are represented on a logarithmical scale along the re-
spective radii. In order to compare the targets and select v, circular
geochemical spectra are made to coincide with respect to the centre
of the smaller circle and similar radii.

To characterize copper ore targets from circular geochemical
spectra, a geochemical index $v = \dfrac{\text{Pb} \cdot \text{Ag}}{\text{Mo} \cdot \text{Co}}$ has been chosen. Its numer-
ical values are relatively constant for deposits of the same formation,
e.g. 1 and 2 or 5 and 6 (see Fig. 112). The values of this index for de-
posits 1 and 6 referred to different formations differ by a factor of

145 600 fold. The value of this index was used to classify ore targets of uncertain origin.

The method of geochemical spectra is employed to determine the differences between similar targets in order to compare different cross sections of one deposits, two or more sections of genetically identical deposits, similar geochemical anomalies, petrographically undistinguishable rocks etc. Tasks that involve multiscale classification of similar geochemical anomalies are successfully solved by computer-aided techniques with the use of factor and cluster analyses, through investigations of correlations between geochemical spectra or matrices of correlation coefficients [34]. To separate similar geochemical data it is a good plan to resort to discriminant analysis, a simplified version of which is a method of geochemical spectra [20].

One of criteria for the classification and evaluation of supergene lithochemical anomalies is their planimetric configuration and modern relief features which is shown by an examination of ore element isoconcentration maps in the dispersion field. If the anomaly axis on a mountain slope cuts contour lines at an acute angle and remains straight passing a valley or watershed, this is a characteristic feature of the residual dispersion aureole of a steeply dipping mineralized zone. If isoconcentrates and axis of the anomaly follow the relief isohypses, this attests to a horizontal occurrence of the mineralized zone. The deviation of the anomaly axis when crossing a watershed or a valley makes it possible to determine the azimuth of the dip of the mineralized zone. If the anomaly shows itself only on one slope and is extended along the gradient of the relief, then its part referred to the lower concave interval of the slope seems to be the tail of the dispersion aureole and is not underlain by primary ore which can be expected only at the upper portion of the anomaly (see Sec. 3.9).

All these features of the geochemical field are manifested provided the isolines are correctly drawn and standard interpolation referred to the shortest distance between the adjacent profiles is not always the best.

The results of the detailed and evaluation operations in the geochemical anomaly zone are used to undertake probe drilling and pitting operations with an objective to uncover and test the mineral in its primary occurrence. It is the invariable practice to reconnoitre secondary residual aureoles if the thickness of unconsolidated sediments is less than 3 m, by excavating ditches. Prospecting pits are less reliable for exploring geochemical anomalies in which case the orebody may be omitted by falling between pits.

Following mining operations or independently of these latter if the geological conditions prevent them, exploratory boreholes are sunk into a geochemical anomaly estimated to be promising. In-

variably, continuous geochemical sampling of ditches, pits and core from boreholes is necessary.

If the characteristics of the mineral discovered by mine workings and the estimation of the prospective reserves of the target meet the requirements of economic importance one should decide on its pre-liminary investigation. The data of geochemical sampling of the primary mineralization help better determine its erosional surface level and prognosticate its depth. Further, geological tasks and par-ticular objectives of geochemical investigations are inferred from the reconnaissance operations. Under less favourable conditions mining operations may discover only an insignificant mineralization. Then, proceeding from its genetic type and local structural and geo-logical setting, one should decide whether it may be assumed to be the supraore primary halo of a hidden deposit (see Fig. 55). To de-cide this, one has to sink new, deeper exploratory boreholes. In either case the success of geochemical investigations is determined by a knowledge of the primary zoning, mechanisms of the origination of supraore halos and other geochemical features of genetically similar deposits.

Sec. 6.2.3. Collection, Processing and Analysis of Samples

No doubt, such methods of geochemical exploration should be considered as the best that permit prospecting to be conducted on the move, without a need to collect samples, with remote or contact continuous determinations of chemical element contents. These in-clude, e.g. gamma spectroscopy, airborn, automobile and pedestrian surveys involving borehole, deep and logging operations during which U (from Ra), Th and ^{40}K contents are determined continuously or at discrete points, at the ground surface or in exploratory bore-holes, generally automatically. No sampling is involved when con-ducting automobile and pedestrian surveys using berillometers, fluo-rometric and phosphorometric neutron activation surveys. It is possible to carry out boronmetric, gaseous mercury aerial and near-surface surveys, laser atmochemical (aerial) and automobile surveys for methane, aerogeochemical surveys for metalloorganic compounds and some others. All these methods differ in terms of their eventual development and practical use for geochemical exploration for min-eral deposits. Some of them are indispensible for solving special tasks (e.g. aerogeochemical prospecting for radioactive ores) or at the stage of detailed surveys and geological appraisal of geochemical anomalies. However they cannot as yet substitute for geochemical surveys with sampling.

What follows is a brief review of well developed techniques of mass sampling, processing and analysing of various lithochemical

samples that were elaborated following the experience gained during
many years.

Dispersion flow lithochemical surveys are conducted to agree to
the local drainage system omitting topographic operations and using
for field records maps on 1/100 000-1/50 000 scales or aerial photo-
graph contact prints (generally on a 1/30 000 scale). At the same time
the samples are collected, when medium-scale lithochemical surveys
of secondary dispersion aureoles are involved, station marks are
established along a system of parallel profiles supported by previous-
ly run geodetic traverses spaced at intervals of 10 cm of the scale
of the survey. Detailed lithochemical surveys on a 1/10 000 and larger
scale rely upon a previously established topographic network
of profiles and station marks. The direction of the profiles is
invariably selected across the strike of ore-controlling struc-
tures.

When conducting exploratory lithochemical surveys of dispersion
flows and aureoles, samples of local silt are collected observing stand-
ard conditions and minimum depth determined by the location of
the representative horizon. Samples are put in previously numbered
bags, the initial mass of a sample being some 200 g.

Surveys are conducted in summer time. The team led by the chief
collector (junior geologist) collects during a working day, depending
on the terrain in hand, 20-30 samples at intervals spaced 500 m apart,
from alluvium, and 100-200 samples from eluvio-deluvium at in-
tervals of 50-20 m. Sample collection may present problems when
operating in the Far North where frost weathering of the mountain-
ous slopes often causes what are known as *kurums*, i.e. a continuous
cover of coarse stone stream. Another likely handicap to sampling
in the aforementioned regions is the presence of the thick blanket
of moss on northern slopes under which permafrost is preserved even
late in summer. In arid zone southern deserts powdered material of
aeolian origin impoverish secondary dispersion aureoles associated
with ore deposits mixing with the eluvio-deluvium. The fine fraction
should be removed from the samples collected in such regions by
screening through a 0.25 mm mesh sieve.

Samples collected during a lithochemical survey are generally
dried and then screened by using a 1.0 or 0.5 mm mesh sieve, the
coarse fraction being thrown out. Studies of a supergene dispersion
aureole from the fine fraction of products of weathering usual-
ly ensure a good reproducibility of the results of a lithochemical
survey.

Exploration referred to primary halo employs continuous sampling
of the walls of underground mines and core of boreholes by a dashed
channel technique by integrating to one sample of 8-10 rock chips
from the specified interval. The general sampling interval length is
2-5 m, and 10-20 m at the periphery of the ore field, the mass of a

sample is 300-350 g. Before attrition these samples are crushed and reduced to weigh 50-100 g.

Whatever the method of geochemical exploration, sampling data are recorded in field books and in case of aerial photographs or plans of mine workings are not used, a rough survey of the terrain is made. To appraise the quality of geochemical surveys monthly control sampling is conducted on the scope of at least 3 % [17].

Analysis of samples is essential for the results of geochemical prospecting. It may use any method that will satisfy the following principal conditions: (1) sensitivity of analysis should be better than pre-clarke values; (2) reproducibility must be sufficient to solve geological tasks posed; (3) promptness of analysis should be high and costs minimum. This list may be augmented by such requirements as a possibility of performing analyses without chemical processing and in field conditions including the use of portable instruments, concurrent determination of a maximum number of elements, a large range of element contents—up to 5-6 and more magnitudes, possible simplicity and objectivity of the documented results, totally automated analysis and direct input of the results into a computer, etc. Some of these requirements are contradictory and hardly compatible, e.g. high sensitivity and accuracy coupled to low costs or portability of equipment and largest possible number of elements to be determined.

The main of the aforementioned requirements were best satisfied by emission spectroscopy which made possible some 50 years ago the origination and effective application of geochemical exploration of mineral deposits. Spectral analysis has not lost its importance for geochemical prospecting, yet the gap between analytical means and requirements put by practical prospecting is appreciable and is increasing. Currently emission spectroscopy for 40 chemical elements by a method of blowing sample fines into a stabilized a.c. arc is performed by using Soviet-built diffraction spectrographs Model ДФС-13 (or ДФС-8) of high resolving power.

In most field laboratories spectrograms are interpreted visually. The analytical data over all content ranges, starting from the sensitivity threshold, are expressed by ten discrete digits for each order: 1; 1.2; 1.5; 2; 2.5; 3; 4; 5; 6; 8. This is in agreement with a logarithmical scale and is *a sine qua non* condition in geochemical exploration. In best laboratories the magnitude of an average relative error of independent control analyses is within $1.25^{\pm1}$-$1.4^{\pm1}$, the permissible value being $1.4^{\pm1}$. The high degree of specialization of operators and division of labour permitted the maximum productivity of major field laboratories of geophysical expedition of Kazakhstan in summer periods which was 2-4 thousand samples every day, the annual number of samples collected attaining 600 000-800 000 [20], sometimes amounting to 1 million samples.

Important disadvantages of emission spectroscopy are insufficient sensitivity of the determination of Au, W, Sb, Ta, Nb, As, P, Hg and the fact that no provision is made for geochemical laboratories to have automatic input of data to a computer. Apart from emission spectroscopy other methods are used.

1. Atomic absorption analysis for mercury is a highly efficient, versatile and the most reliable method extensively used for whatever geochemical surveys including analysis of solid, aqueous and gaseous samples and also vegetation samples without reduction to ashes. Determinations are made referring to the intensity of the absorption of the resonance line of mercury 253.7 nm in the gaseous phase of the sample being analysed. Mercury atomization, during solid-phase sample analysis, is carried out by using a specimen 0.5-1.0 g heating it to 700°, the radiation source being provided by a quartz mercury lamp. During the analysis mercury vapours are previously deposited on Au sorbent followed by automatic desorption and measurement of its contents with visual digital or pen-recorded readout.

2. Chemical adsorption analysis for Au followed by emission spectroscopy finishing suggested by N.I. Safronov in 1955 is being extensively used in the USSR and other socialist countries. The limiting sensitivity of determinations is $5 \times 10^{-7}\%$ Au which is somewhat less than is necessary. This type of analysis is employed in this country for all aurometric surveys and has made possible all major discoveries of ore deposits of economic value.

3. Atomic absorption flame spectral analysis for a wide range of ore elements relies on the measurement of the intensity of the absorption of monochromatic radiation of the given element by vapours of the sample being analysed introduced into the gas torch flame as a solution. The source of radiation is provided by sets of special tubes with a hollow cathode, generally for three ore elements each (say, Cu, Ni, Co). When doing analysis for a single element, the capacity attains 600 determinations per hour. Being inferior to emission spectroscopy in terms of technological and economical characteristics, this method has almost identical sensitivity and much better accuracy.

4. Nuclear physical methods of the determination of one particular element contents. These include photoneutron analysis for beryllium relying on the nuclear reaction $^9Be + \gamma$ quant $\rightarrow$ $^8Be + n$. Beryllium nuclei manifest the least neutron binding energy—1.666 MeV, the closest low threshold of photoneutron reaction is exhibited by deuterium—2.226 MeV. By irradiating samples or rocks *in situ* by γ-rays with an energy greater than 1.666 but less than 2.226 MeV it is possible to ensure high selectivity of the photoneutron reaction for Be. Such a source is provided by the radioactive isotope ^{124}Sb with radiation energies in the range 1.7-2.1 MeV. Neutron emission is measured by using proportional counters.

The neutron activation method using a Po-Be source determines fluorine contents and, indirectly, phosphorus contents. The method is based on the nuclear reaction ^{19}F $(n, \alpha)^{16}N$ occurring on fast neutrons. The gamma-radiation of the short-lived isotope ^{16}N is measured by the use of a scintillation spectrometer. The sensitivity of determinations during blasthole fluorometric survey without sample collection is 0.1% F, i.e. sufficient for mining purposes only. Analysis of samples for P is based on the close correlation between its content with F content in phosphorites the principal mineral of which is fluoapatite $Ca_5[PO_4]_3F$.

Neutron activation analysis for gold from isotope ^{198}Au with the lower than clarke value sensitivity $n \times 10^{-8}$% is conducted by using powerful neutron sources.

5. X-ray spectroscopy (XRS) is finding more applications in geochemical prospecting. The method relies on the irradiation of a material by γ-quanta and measurement of the characteristic secondary emission of the elements. The advantages of XRS are the simple and small-bulk equipment convenient for use in field conditions.

In XRS atoms are excited at K- and L-levels of the electron shell. Isotope sources, less commonly portable X-ray tubes are used for irradiation. The most intense lines of the characteristic emission of K-series—α_1 and α_2, of L-series—α_1 and β_1 are measured. The gamma secondary emission is recorded by means of scintillation, proportional and semiconductor counters. Two-channel devices РРША-1, РРК-103 "Poisk", one-channel devices БРА-6, РПС4-01 "Gagara", РРК-102 "Mineral-6" and others are being marketed specially for XRS methods of geochemical prospecting.

Prompt XRS analysis in field conditions is conducted by determining the total sum of the chalcophile element content with close energies of the characteristic emission. The threshold of the determination of the sum of chalcophile elements by XRS is 0.005-0.01%, the principal contribution to X-ray secondary emission being made by Cu, Zn, Pb and As.

It is plausible to resort to XRS at the stage of detailed lithochemical surveys when it is desired to appraise geochemical anomalies of a known element composition. XRS cannot substitute for other methods of analysis during small-scale geochemical surveys.

6. These few recent years have witnessed a renewed interest in ion selective electrodes that were used for geochemical exploration as early as 1932-1937 [29]. The undisputable advantages of spectral analysis were responsible at that time for the discontinuation of experiments on these electrodes. However, progress made in their practical applications calls for a reconsideration of the problem.

In the immediate future one may well expect the origination of utterly novel methods of measuring the geochemical field that are likely to enhance the efficacy of prospecting. Yet routine practice

should not neglect classical straightforward methods of field chemical and mineralogical analyses. When carrying out a geological survey of residual Pb dispersion aureoles and recording field books of prospecting ditches excavated within their contours it is perfectly obligatory to resort to field microchemical reaction for Pb by using a 10% solution of HNO_3 (solvent) and a 3% solution of KI (developer). The efficiency of this elementary reaction is superior to any portable analyser of the latest models.

In any case, it is desirable that sample analysis be conducted as close as possible to the site of field operations and their results be obtained immediately after sampling. This justifies attempts to make mobile field laboratories using buses and trailers with autonomous power supply. In uninhabited regions this technique may prove most efficient. However, their movement is limited by passability, and if the sampling grid is sparse, it is always reasonable to take samples to a laboratory than to move the laboratory to sampling points. It is only geochemical surveys without sample collection that can solve the problem of analysis terms.

Analysis of samples should yield results as soon as possible which is sometimes erroneously connected with immediately undertaking a detailed survey of each discovered anomaly. Such an approach is inconsistent with rational survey practice. If the geological assignment envisages geochemical exploration of a vast region, it is necessary to proceed to detailed surveys of anomalies after 30-40% of the total area has been surveyed thus making possible a comparative evaluation of the data obtained.

Various methods of prompt analysis of samples used in geochemical prospecting may differ to some degree or another in terms of complexity and time taken. However, that it is possible to obtain the results of sample analysis on the same day, after a month or in half a year is not the feature of the given method of analysis but is entirely governed by the organization of operations concerned.

A separate problem not associated with mass analysis of geochemical samples is a study of modes of occurrence of ore elements in geochemical anomalies of various genesis. In order to determine the mineral composition of lithochemical dispersion flows and residual aureoles of the fraction of ore elements represented by heavy stable minerals use is made of heavy concentrate analysis after washing in a trough of 10-12 kg of alluvium from C'_{max} points or eluvio-deluvium from an area of C_{max}. Heavy concentrate analysis, however, cannot be used for studying salt aureoles or the light and finest fractions of the mechanical component. The usual practice was to tackle such problems by methods of phase chemical analysis the results of which cannot be considered to be unambiguous.

The advent of electronic microprobes has opened up new possibilities in this field [26].

Geochemical exploration for mineral deposits is unvariably a scientific investigation and, as we use one kind of analytical procedure or another in routine work we should bear it in mind that a better method is sure to exist.

Sec. 6.2.4. Estimates of Expected Reserves

Expected reserves of materials of interest to us according to confidence categories P_3, P_2, P_1 are evaluated from the results of geological, geochemical and geophysical investigations jointly with mining and drilling operations. Of particular importance are geochemical data proper that are expressed in terms of contents of the valuable component in question. Reconnaissance geochemical surveys of successively increasing detail jointly with computerized handling of the observed data allow repetition of these calculations at different stages of exploratory work. The decisive role for the evaluation of expected reserves is played by genesis and geological setting of the discovered deposits. By assuming that all geological data have been taken into consideration, we will consider quantitative characteristics necessary for a substantiation of these estimates in geochemical terms.

Quantitative interpretation of the data obtained by regional, reconnaissance and detailed lithochemical surveys obeys successive consideration of metal contents in geochemical anomalies—dispersion aureoles and flows, their productivities and metal reserves in targets of search of progressively increasing confidence (Table 26). Basing on this sequence it is possible to elaborate a scheme of interpretation of the data when alternative techniques of geochemical prospecting are involved.

The quantities entering the relationships from which expected reserves of all three categories are calculated, excepting the depth H, are unambiguously determined by lithochemical surveys. Methods of their evaluation have been discussed in detail. For relatively steeply dipping (other than horizontal) lodes the calculation depth is selected from geological data by taking into account the genetic type and erosional surface of the mineralization or is limited by a predetermined interval. Clearly, the adequacy of the evaluation of expected reserves is very much governed by the chosen calculation depth. However, the principal reasons why prognosticated estimates during geochemical prospecting prove unsubstantiated are unfavourable morphological conditions of the mineralization, low and nonuniform metal contents, sometimes systematic overestimation of the results of spectral analysis. Sometimes the wrong idea of the configuration and geological structural conditions of occurrence of orebodies may lead to the unwarranted cessation of prospecting operations after unsuccessful exploratory workings and boreholes failed

TABLE 26

Sequence of Considering Parameters of Lithochemical Dispersion Flows and Aureoles [25]

Num-ber	Parameter	Units of measure-ment	Formula
1	Maximum metal content	%	C'_{max}; C_{max}
2	Amount of metal in dispersion aureole along profile (linear productivity)	m %	$M = \Delta x \left(\sum\limits_{x=1}^{n} C_x - nC_0 \right) = M_p k$
3	Productivity of dispersion flow	m^2 %	$P' = S_x (C'_x - C'_0) = k'P$
	Productivity of dispersion aureole	m^2 %	$P = \Delta x 2l \left(\sum\limits_{x=1}^{N} C_x - NC_0 \right) = kP_p$
	Amount of metal per metre of depth	t/m	$q' = \dfrac{P'}{40}$; $q = \dfrac{P}{40}$
4	Expected reserves:		
	P$_3$	t	$Q'_H = \dfrac{1}{k' \times k} \times H \sum\limits_{i=1}^{m} q'_i$
	P$_2$	t	$Q_H = 1/k \times q \times H$
	P$_1$	t	$Q^*_H = \alpha 1/k \times q^* \times H^*$

to yield relevant information thus preventing a correct estimate of the expected reserves from being made. There are cases when the original geochemical estimates were substantiated by repeated mining work.

By choosing the value H within reasonable (and sufficiently moderate) intervals, followed by a comparison of the expected reserves with the established values that can be limited by this very depth whatever the depth to which the economically important mineralization has been investigated. That is why the calculated prospective reserves Q'_H and Q_H, lacking other data, are often limited to a depth 100 m for Be, Co, Ta, Ag, Au, Hg, Bi deposits and 200 m for F, P, Ni, Cu, Pb + Zn, Nb, Mo, W, Sn, Sb deposits. Eventually estimates Q_{100} or Q_{200} may be increased by an even number of times, depending on the more accurately determined data on the depth of the mineralization. This reduces to the minimum an overestimation of reserves owing to unduly increasing the calculation depth.

Estimates of expected reserves by using the above relationships in a sheet fashion to a depth H are equivalent to calculations in a triangular fashion to a depth $2H$. Calculations to predetermined depths 100 and 200 m are consistent with concepts of the wedging out of ores at depths 200 and 400 m, respectively, usual for medium-size deposits. When conducting geochemical exploration, the discovery of large-size deposits whose ores may be traced to much greater depths is not ruled out. The extension of an economic mineralization from the ground surface to a depth 1 000-1 200 m and more for large deposits of nonferrous, rare metals and gold is common occurrence. Consequently, calculated data to the aforementioned predetermined depths that can be described as cautious for targets of search exceeding medium-size deposits are sure to be underrated. As a result, estimates of expected reserves aimed at adequately directing exploratory effort will be of no use. That is why it is worthwhile varying the depth of calculation, i.e. increasing it if a large deposit is expected, and decreasing if a small orebody is to be discovered. It is convenient to use as a geochemical criterion for this choice the areal productivity of the mineralization P_p (in m²%) and it is this approach that is implemented in the acting Manual [17].

In conformity with the principle of geometrical and geochemical similarity of genetically analogous targets of different size groups we have

$$H_{i\,tot}/H_{tot.\,std} = \sqrt{P_{p\,i}/P_{p\,std}}$$

where $H_{i\,tot}$ and $H_{tot.\,std}$ are extensions of the i-th and standard deposits to a depth interval from level 0.2 to 0.8.

By taking as a standard deposit a small size deposit with specified parameters it is possible, from the productivity of the deposit to be evaluated, to determine its expected depth. The real depth of calculation H_i is governed by the erosional surface of the mineralization $z > 0.2$ and, by virtue of Eq. (107)), will be less than $H_{i\,tot}$. Given a supraore erosional surface of the deposit, the value $(P_p)_i$ should be referred to level 0.2 in conformity with Eq. (105).

The depth of calculation of expected reserves as a function of the mineralization productivity may be determined analytically. By defining $H_{tot} = \beta\sqrt{q_p}$, for $z = 0.2$ we have

$$Q_H = \beta q_p \sqrt{q_p} \qquad (110)$$

where

$$\beta = H_{tot.\,std} \sqrt{\frac{H_{tot.\,std}}{Q_{tot.\,std}}} \qquad (111)$$

Here $q_p = \dfrac{P_p}{40}$ is the productivity of the primary mineralization at a level of its stable values ($0.2 \leqslant z \leqslant 0.8$) in tonnes per metre of depth increment. Given standard figures of total metal reserves and

total extent of the ore interval for a standard deposit of the particular genetic type, it is possible to find numerical values of β. Depending on the stage of exploratory work, q_p may be determined through the total productivity of adjacent dispersion flows $\sum_{i=1}^{m} P'_i$, hrough productivity of secondary dispersion aureoles P or directly from the magnitude of the primary mineralization productivity P_p, including the supraore cross sections of the primary halo by resorting to relevant conversions. For geometrically similar figures the numerical values of β are independent of the size group of a deposit. The advantages of Eq. (110) are versatility and simplicity. Having decided on an adequate model, we will not have to resort to repeated subjective decisions as to the reasonable depth of calculation H which are likely to incur variable errors.

Equation (110) is valid when calculating, given the level of the erosional surface of the deposit 0.2. In other cases the difference should be accounted for. When conducting dispersion flow lithochemical surveys on a 1/200 000 scale to directly determine the erosional surface of the mineralization is not only a difficult but also unreasonable task for the entire area of the discovered deposit which may be more than 100 km². Whatever the results of estimates of z, a new target of search manifesting a large value of $\Sigma P'_i$ should necessarily be further investigated by conducting secondary dispersion aureoles lithochemical surveys. Therefore at the initial stage of geochemical exploration it is permissible for the entire target to take z as being equal to 0.5 in the belief that within a vast ore field tectonic blocks with different value of $\bar{z}$ may be encountered. In more detailed lithochemical surveys referred to secondary dispersion or primary halo it is necessary to determine the level of the erosional surface.

When estimating P_3 and P_2 category reserves a geological survey of the mineralization area *in situ* must be conducted. P_1 category reserve estimates require that orebodies be uncovered and ores in primary occurrence be tested. The acting instructions recommend that estimates of expected reserves be rounded off to the first significant digit. This requirement is inconsistent with the decimal, i.e. logarithmic classification of deposits according to reserves and prevents estimates from being equally accurate within each decade. It is better to round off to the next nearest digit: 1; 1.2; 1.5; 2; 2.5; 3; 4; 5; 6; 8, very much like dealing with discrete values adopted for results of emission spectroscopy.

Sec. 6.3. Prospecting for Oil and Gas Fields

Geochemical exploration for natural gas and oil deposits relies on a theory of sedimentary migrational genesis of oil according to which dispersed organic material of sedimentary rocks where ap-

preciable areas of the earth's crust were subjected to downwarp during continuous time periods provides a source of the origination of hydrocarbons (HC). Dispersed HC are present in various quantities in all stratisphere rocks determining their universal abundance in background contents in the geochemical field. The migration of liquid and gaseous HC from parent rocks to collector seams and traps, is responsible for the formation of gas and oil deposits. Concurrent and subsequent dispersion of HC gives rise to geochemical anomalies over the deposits in a solid, liquid and gaseous phases. The migration of HC of a gas and oil deposit through overlying rocks changes their physicochemical characteristics and the gaseous composition of the subsurface atmosphere, leads to the origination of a zone of abnormally high microelement contents and causes new mineral assemblages. Geochemical exploration for oil and gas (GEOG) is being conducted by pinpointing these anomalies by using varous surveys. The presence of gas and oil deposits is only one of the factors responsible for the origination of geochemical anomalies in a HC field, so the discovered anomalies should be estimated by taking into account geological and geophysical data. Different types and scales of geochemical surveys for oil and gas deposits and also the dimensions of districts to be investigated were presented in Table 22. When medium scale and detailed surveys are involved, reconnaissance geochemical exploration operations are directed to several horizons testing concurrently the core and drilling mud from boreholes.

Atmochemical surveys consisting in the determinations of HC contents in gases are the most important methods of GEOG. Figure 87 showed a scheme of the origination of a gaseous dispersion aureoles over an anticline type oil deposit as a "straight" and a "ring-shaped" anomaly versions. The number of oil and gas deposits of other than anticline type is only 5-6% in this country. In some regions of the USA the fraction of oil and gas yielded by such deposits is 17 to 80% [2]. The role played by geochemical exploration for deposits that are not associated with anticline folds is appreciably higher. The theory of diffusion-induced origination of gaseous dispersion aureoles that was popular during a lengthy time period has been recently augmented by a theory of infiltration-induced anomaly formation. That the processes of infiltration and diffusion go hand in hand is validated by the rapid origination of hydrocarbon anomalies over underground man-made gas storages.

Methods of geochemical exploration for oil fields emerged in the USSR at the same time that geochemical prospecting for ore deposits was proposed. At the present time, however, the state of the art, scope and role played by the two methods in geological prospecting are essentially different. Apart from geological methods, the decisive role in search for oil and gas deposits and identification of oil-bearing structures for deep drilling is being currently played by methods of

geophysical prospecting, mainly seismic and gravimetric surveys. Modern methods of seismic surveys make possible the high detail of construction of structural geological profiles to a depth of several kilometres whereas the results of geochemical prospecting are much less impressive.

This is what was responsible for the subordinate role of geochemical surveys when prospecting for oil fields. Until recently nonscale surveys were mainly conducted on numerous separate spots or along a series of profiles and test methodical operations not supported by a regular grid.

The importance of geochemical exploration to enhance the efficacy of search for oil and gas fields is what was responsible for a revision of previous procedures and gave rise to regular surveys of vast areas. At present one is well aware of the necessity to conduct fourfold geochemical prospecting for oil and gas [2, 11, 12]: (1) regional orientation geochemical surveys on scales 1/1 000 000-1/500 000; (2) reconnaissance prospecting surveys on a scale 1/200 000; (3) exploratory evaluation surveys on a 1/50 000 scale; (4) detailed surveys on a 1/25 000 scale and non-scale operations (Fig. 113). The four-step exploratory cycle has not as yet been tested in any oil and gas-bearing basin (OGBB) [11]. Note that a three-step prospecting surveys according to a 1/200 000 → 1/50 000 → 1/10 000 scale scheme is consistent with the experience gained during many years of work in ore regions. Practical work in foreign countries, especially in the USA, leans heavily on methods of GEOG elaborated by Soviet scientists.

Procedures used in GEOG vary depending on the particular stage of prospecting. *The first* stage consists in atmochemical (gaseous) surveys with determinations of methane and HHC contents in moderately deep (25-30 m) boreholes by using a (5-10) × 2 km grid. In these recent years laser atmochemical automobile and airborn surveys have been conducted at this stage.

The geochemical laser laboratory ГЛА-1 designed at the Institute of Nuclear Geophysics and Geochemistry (in the USSR) mounts on a ГАЗ-66 truck and permits continuous methane content determinations in samples collected from the near-ground atmosphere at a speed 50 km per hour. The sensitivity of equipment is $10^{-5}\%$ CH_4, the speed of response being 10 s which allows reliable recording of methane background content and satisfactory reproducibility of the results to be attained. Automobile atmochemical surveys on a route Moscow-Tashkent have discovered a series of regional gaseous anomalies associated with major geological structure elements. The results obtained provide proof of the plausibility of such studies. Automobile geochemical surveys, however, are limited by the trafficability of the areas to be explored. Laser airborn geochemical surveys that are particularly efficient when it is desired to conduct regional orientation surveys of OGBB are free from these limitations.

18*

Laser methods of probing the atmosphere were first used for ecological studies with an objective to find out the sources of environmental pollution (CO; SO_2; Hg) and to locate leakages from gas pipe

Stage	Targets of search		
	In plan	In profile	Description of target
I	OGB		·Part of sedimeted fill of PGB
II	Zone, area		Upper geochemical zone between first water and gas resistant layer and ground surface
III	Local area		Part of lower geochemical zone
IV	Productive area		
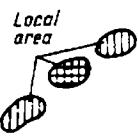
a b

⊡ 1   ⊞ 2   ⊞ 3   ⊠ 4   ⊞ 5   ⊞ 6   ⊟ 7

FIG. 113. Targets of search during geochemical prospecting for oil and gas fields [10]:

1 — foundation rocks; 2 — target of geochemical exploration at particular stage; 3 — target singled out for eventual operations; 4 — hypothetical (a) and discovered ¦(b) regions of borehole sites; 5 — upper geochemical zone; 6 — lower geochemical zone; 7 — first regionally persistent water and gas resistant horizon

lines. Various laser sources and methods of detection of indicator gases have been proposed for mineral exploration. Currently, the CH_4, HHC, H_2S, SO_2, I_2, Hg and other gases contents in the atmosphere are determined accurate to the clarke values. For geochemical

prospecting for oil and gas these methods were implemented as laser methane surveys two versions of which are shown in Fig. 114.

The airborn geochemical and mobile laser surveys using topographic reflectors or special mirrors (see Fig. 114a) consist in the measurement of the relative intensity of reflected emission of two adjacent wavelengths of the emitter, λ_1 and λ_2, of which λ_1 corresponds to
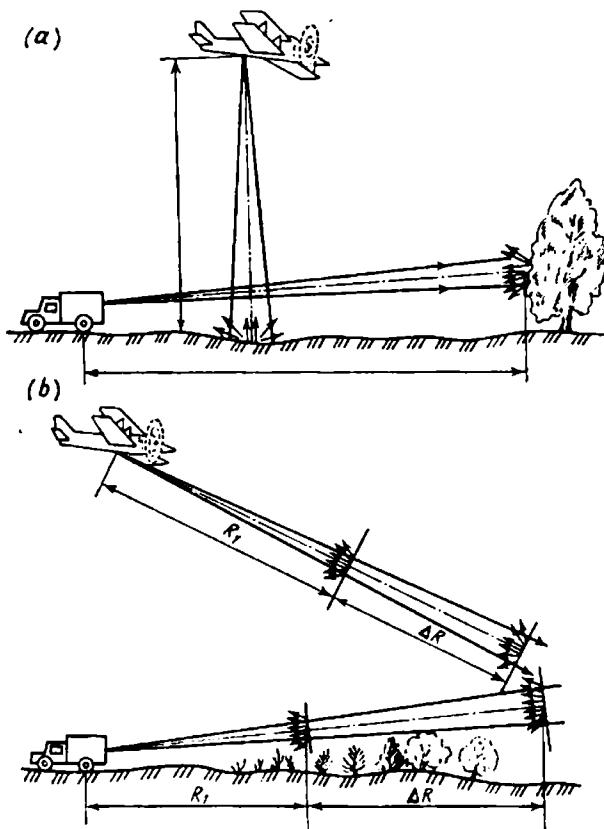
FIG. 114. Laser geochemical survey. After I.M. Nazarov et al.:
a — using topographic reflectors; *b* — measuring scattered reflected beams

the line of resonance absorption of the gas being determined, λ_2 lying beyond its limits. Measurements by using two close wavelengths rule out the effect of fluctuations of the atmosphere's composition. The method of scattered emission (see Fig. 114b) consists in the measurement of the intensity of two similar laser pulses λ_1 and λ_2 scattered back by aerosols present in the atmosphere at the front (R_1) and rear ($R_1 + \Delta R$) boundaries of the portion of the atmosphere being tested.

The distances R_1 and $R_1 + \Delta R$ from the emitter are determined by the time lag of the returning laser pulses. An automobile laser geo-chemical survey by using a mirror reflector on a profile across the Anastasievsko-Troitskoye gas and oil deposit discovered a distinct methane anomaly extending about 2 km. Laser aerial geochemical surveys were successfully conducted over a vast area north east of the Caspian Sea. Arid zone regions are especially favourable for atmochem-ical, including airborne, surveys; over bogged areas appreciable methane-induced disturbances occur. Work is in progress in the USA to conduct spatial remote prospecting for gas and oil by determining the iodine content in the near-ground atmosphere from the optical spectrum of the solar rays reflected by the earth. Relevant studies of oil compositions suggest that abnormally high iodine contents in the near-ground atmosphere may serve as guide to deposits of hydro-carbons at depth [2].

The second stage of geochemical prospecting for oil and gas fields involves identical atmochemical surveys with sampling depth up to 30 m on a 1/200 000 scale of areas manifesting abnormally high con-tents of indicators to oil and gas deposits or structural uplifts. With-out substituting for these terrestrial surveys they may be augmented by airborne and/or automobile surveys on the same and closest larger scale. Atmochemical surveys carried out at this stage may sometimes be added to by hydro- and lithochemical studies. Hydrochemical guides to oil fields are sulphate-free waters, high iodine contents and dissolved HC contents in water. It is the purpose of prospect-ing reconnaissance surveys to determine areas for staging exploratory evaluation geochemical work followed by exploratory drilling.

The third stage of search for oil and gas fields involves atmochem-ical surveys of areas assumed as being oil-bearing that are conduct-ed at several reference horizons below the zone of active attack of methane oxidizing bacteria and atmospheric oxygen in the depth range 30 to 200 m. Surveys are carried out on a 1/50 000 scale, the number of samples at a sampling point being 5-20 including testing core, drilling mud and stratal waters. Apart from methane and HHC contents, hydrocarbon-free gases (CO_2, H_2, He, Ar, H_2S) contents are determined and bituminologic hydro- and lithochemical studies are undertaken.

The first from the ground surface representative horizon for this type of geochemical exploration is considered the upper water and gas resistant horizon regionally persistent along the profile of the oil and gas bearing basin. Atmochemical surveys at the prospecting evaluation stage are conducted so as to test the entire thickness of the representative horizon. Once local abnormally high gaseous HC contents are discovered, additional surveys of two-three reference hori-zons lying below the first one are carried out. The depth of penetra-tion may, if necessary, be 600-700 m. The atmochemical survey of a

profile across the Karazhambas, West Kazakhstan, oil field deter-
mined CH_4, total HHC and He contents in core samples taken from
shallow (25-30 m) boreholes spaced at interval 800-400 m. Graphs
showed the location of the oil deposit and tectonic faults by abnor-
mally high gaseous component contents. Mercury vapour anomalies
were discovered in the soil air samples collected from 1-2 m deep
auger holes above the Palyanovskoye oil deposit, the depth to the
deposit being 2 500 m [9].

The fourth stage consists of detailed geochemical surveys on a
1/25 000 or without scales, the number of samples for a sampling
point amounting to 20-60. The objective of the survey at this stage
is to optimize the location of exploratory boreholes within the bound-
ary of the discovered gas- and oil-bearing structure and to decide
on points for sinking deep boreholes.

Reconnaissance geochemical prospecting undertaken in 1970-1980
in the USSR discovered 320 anomalies suggestive of oil deposits 46
of which were tested by deep boring. 80% of drilling operations yield-
ed favourable results. Such an efficacy was largely made possible
by the fact that most of the recommendations by geochemists agreed
with those proposed by geophysicists [11].

Lithochemical surveys offer most promise for the eventual develop-
ment of methods and procedures of geochemical exploration for gas
and oil deposits. The duration of migration of HC from a gas and
oil deposit is commensurate with its lifetime and is responsidle for
important mineralogical geochemical transformations of overburden.
Hydrocarbons participating in redox processes cause pH to in-
crease and Eh to diminish which gives rise to new mineral formations
and redistribution of minor elements. Unlike gaseous anomalies that
are illustrative of the dispersion aureole, the lithochemical anomalies
are an integral result of a process that was at work for a lengthy time
period. Mineral neogenesis in the rocks overlying oil fields may in-
clude sulphidization, silicification, carbonatization, dolomitization,
accumulation of radioactive elements, Mn, V, Pb, Cu, Co, Ba and
some other minor elements. Convincing evidence of the importance
of carbonate surveys for the exploration of oil deposits has been pub-
lished in the USA. 38 years of such surveys covering an area 320 thou-
sand km^2 (875 thousand soil assays) has discovered 160 geochemical
anomalies. Testing these by drilling results in opening of 38 oil and
gas-bearing structures. Modern methods of computerized handling
of the observed results may appreciably enhance the efficacy of litho-
chemical exploration for deep-seated oil and gas deposits.

Conclusion

Further perfection of the theory and extensive application of geochemical exploration for mineral deposits are problems that have many aspects and are self-evident. What is needed is to further enhance the geological and economic efficacy of geochemical prospecting wherever it is being conducted and to enlarge the spectrum of materials for the search of which these methods may be used. First and foremost, it is necessary to direct geochemical exploratory effort toward greater depths in whatever geological setting and landscapes and to increase the confidence level of the estimation of geochemical anomalies discovered. The latter task will call for the improvement of the available and elaboration of new, more accurate methods of appraisal of prospective reserves of materials of interest to us by taking into account the genetic features and geological and structural conditions of occurrence of principal economically important deposit types.

The next few years will witness an ever increasing scope of geochemical exploration following the standard procedures to be conducted on various scales and with different purposes. Lithochemical dispersion flow surveys on a 1/200 000 scale will have to be completed and regular lithochemical secondary dispersion aureole surveys on 1/50 000 and larger scales continued in orebearing regions in Siberia and the North East of the USSR. In Asian, African and Latin American countries orientation lithochemical surveys will have to be carried out in the same sequence starting from a 1/1 000 000 scale encompassing territories that are less known geologically.

In the years to come, geochemical prospecting for concealed deposits by locating their superimposed dispersion aureoles on the surface of the overburden including haloid aureoles will be conducted at increasingly higher rates at covered areas with a limited thickness of the overlying sediments including traditional mining areas of the USSR and other developed countries. Search for concealed orebodies within the contours of economically important deposits will be continued by pinpointing primary halos associated with them jointly with detailed surveys of the primary zonality of well-known (standard) deposits. Finally, various geochemical surveys will have to be undertaken such as to more extensively encompass vast areas

where oil and gas fields are likely to occur much as in the effective search for mineral deposits.

The large volume of reconnaissance geochemical exploration will require changes in the methods that are available now. The atmochemical method of search for ore deposits is certain to be rapidly improved on by using novel analytical procedures including direct determinations of heavy metal vapours and the elaboration of highly sensitive devices based on principles borrowed from bionics. Progress in geochemical methods of exploration can be made possible by radically improving analytical procedures needed for this work. This can be attained only by resorting to fully automated neutron activation analysis of lithochemical samples with a direct input of the observed data to the computer memory. The same is true of automation of gaseous, particularly chromatographic, laser and mass spectroscopic analyses of atmochemical samples. Provided that there is no more gap between sample analysis and input of the data obtained into a computer it will be possible to introduce an automated system of processing of the geochemical data. Extensive automation of acquisition, processing, storage and mapping of the survey data, including preparation of polychromatic and three-dimensional geochemical maps and cross sections is an urgent task to be solved in the immediate future.

The next few years should witness successful optimization of decisions taken during geochemical exploration which will cause one to resort to linear programming, strategic game theory and other special aspects of modern mathematics. To sum up, there is a multitude of possibilities to further develop and introduce geochemical exploration techniques. Tasks that have to be solved are legion which makes investigations in this domain most efficient and exciting.

The theory of geochemical exploration for mineral deposits is one of the most dynamic subdivisions of geological disciplines. This is evidenced by scientific activities in this field that are mirrored by the numerous national and regional conferences and seminars held in different cities in this country and abroad. A special subsection on geochemical methods of prospecting was part of the 27th session of the International Geological Congress that was held in Moscow in 1984.

Some young geochemists erroneously believe that the determination of forms of occurrence of As in a limonite sample is science, whereas analysis of the data on 12-15 ore element contents in 100 thousand geochemical samples presents a routine geological operation which is far from being true science. The fallibility of such concept is quite evident. The impressive bulk of information contained in the objective data obtained by geochemical prospecting surveys calls for a profound mind and analytical capacity of a scientist. If, in addition, the thorough geological, geochemical and physico-

mathematical interpretation of these data should result in the dis-
covery of a large deposit of economic importance, this will bring the
scientist a profound satisfaction. Names on the map of the USSR —
Bilibin, Gubkin or Lutugin are due to Yu.A. Bilibin (1901-1952),
I.M. Gubkin (1871-1939), L.I. Lutugin (1864-1915). These localities
were named so not only because these men of science were, like many
others, great geologists. This is a tribute to their work that made
famous the country for its mineral wealth.

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